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HYDRATION OF PORTLAND CEMENT

BY

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and

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Bureau of Standards

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By A. A. Klein and A. J. Phillips

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I. INTRODUCTION

The Geophysical Laboratory,[1] studying the ternary system, lime-silica-alumina, has established the constitution of all the definite combinations of lime and alumina, lime and silica, silica and alumina, and lime, silica, and alumina. Furthermore, this laboratory [2] has verified the work of the Geophysical Laboratory,

[1] J. Ind. Eng. Chem., 3, pp. 211–227; April, 1911.

[2] Concrete-Cement Age, 2 (cement mill section), pp. 3–7; January, 1913.

and determined the compounds which are actually present in Portland-cement clinker. With the constitution of cement thus established, it was thought advisable to take up the study of the effect of various amounts of water and steam at atmospheric and higher pressures on the individual compounds of cement and on Portland cement itself.

The work consisted of the preparation of the constituent binary compounds, their hydration on microscope slides with an excess of water, their hydration in a cylinder with steam according to the method proposed by Bied,[3] their hydration in the autoclave with steam at various temperatures and pressures, and the hydration of specimens molded with quantities of water approximating those used in normal consistency mixtures; all products thus formed being examined with the petrographic microscope to determine the changes taking place.

The treated products were the three aluminates, monocalcium aluminate ($CaO.Al_2O_3$), 5:3 calcium aluminate ($5CaO.3Al_2O_3$), and tricalcium aluminate ($3CaO.Al_2O_3$); four silicates, calcium metasilicate ($CaO.SiO_2$), gamma-calcium orthosilicate ($\gamma 2CaO.SiO_2$), beta-calcium orthosilicate ($\beta 2CaO.SiO_2$), and tricalcium silicate ($3CaO.SiO_2$); free lime burned at different temperatures, a high silica cement, a low silica cement, a high iron cement, and a high magnesia cement. In addition to the above two white cements containing different percentages of water due to aeration were studied. Previous papers [4] [5] of this laboratory have shown that the magnesia enters into beta-calcium orthosilicate up to 6 per cent and into tricalcium aluminate up to 10 per cent, forming homogeneous compounds; also that cements containing 7.5 per cent magnesia show no distinctive magnesium compounds. Therefore in this work no silicates and aluminates containing magnesia were prepared, but commercial cements of high magnesia content were examined.

[3] Proc. Int. Assoc. Testing Mat., 2 (9), p. 8; 1911.
[4] Orig. Com., 8th Int. Cong. Applied Chem., 5, pp. 73–81; 1912.
[5] Concrete-Cement Age, 4 (cement mill section); pp. 29, 33, 38; March, 1914.

II. ALUMINATES

1. PREPARATION OF COMPOUNDS

For the preparation of specimens of aluminates, chemically pure calcium carbonate and alumina were mixed in desired proportions with a little water, molded into hollow bars, and burned in an updraft kiln. A diagram of this is shown in Fig. 1. The furnace was built of common brick and the chamber lined with magnesite brick. The specimens rested on a horizontally placed brick and were heated by two Fletcher burners supplied with natural gas and compressed air, a thermocouple and galvanometer being used to control the temperature. The furnace was usually fired overnight with natural draft, the temperature[5a] reaching 800–900° by morning. The blast was then turned on, and in three to four hours the temperature was raised to that desired. Owing to the fact that the compressed air, and, in later work, the electric current, could be obtained for only eight hours a day at a maximum, it was impossible to bake the specimens continuously until a microscopic examination showed the desired homogeneity. Instead, the material was usually burned for one day, ground, examined, remolded and reburned, this process being repeated until the sample was satisfactory as regards homogeneity. Not over 400 grams of raw material were burned at one time. The resultant product was pulverized and sifted through a 200-mesh sieve before hydrating.

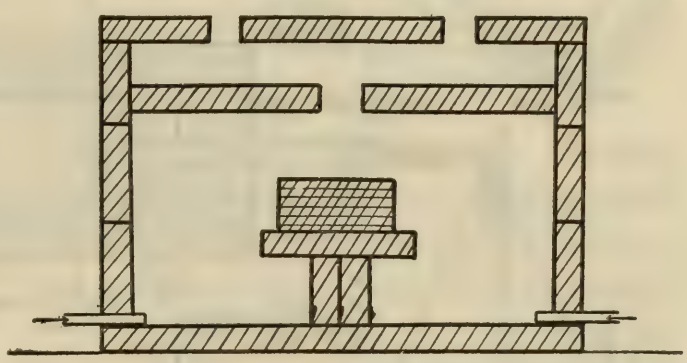

FIG. 1.—*Showing up-draft kiln*

In no case was it possible to secure a homogeneous product by one burning in the furnace. At least two burnings with intermediate grindings were necessary. This must be borne in mind in view of the comparisons which are made with the results of other investigators of this problem, since, with few exceptions, they

[5a] All temperatures in this work are given in the centigrade scale.

made no reburnings and no petrographical examinations. Consequently it is doubtful whether their products were homogeneous and has the desired constitution.

2. DESCRIPTION OF APPARATUS

The slides for observing hydration with excess of water were prepared in the following manner: A very small amount of the material to be hydrated was placed on a plane (not concave) slide, mixed with an excess of water, and covered with a thin cover glass.

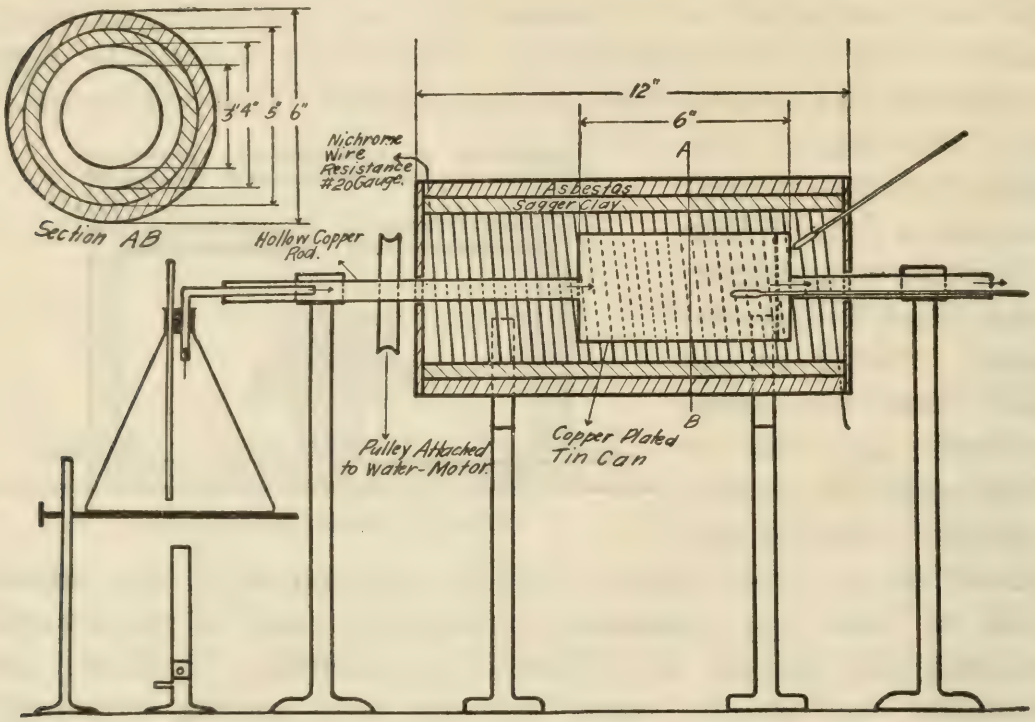

FIG. 2.—*Showing apparatus for hydration in steam*

Pressure was then applied on the latter so as to completely eliminate air bubbles, and the sides were carefully coated with a solution of Canada balsam in benzol or xylol (preferably the former because it evaporates more quickly). By this means evaporation and carbonation were prevented.

The apparatus (see Fig. 2) used for the hydration in steam at normal pressures consisted of a tin cylinder, through an opening in each end of which projected copper tubes. The cylinder was revolved in a nichrome resistance oven by a water motor at a speed of 20 revolutions per minute. The temperature inside this

cylinder and between the cylinder and the oven was read by means of mercury thermometers. The control of the temperature was rather difficult, owing to an endothermic reaction which started about 15 minutes after steam was first passed over the material; the inside thermometer in some cases showed a temperature of 100–105°, while the one outside the cylinder showed as much as 200°. Opening and closing the switch in the line supplying the current at intervals presented the most satisfactory method of regulating the temperature.

The autoclave consisted of a piece of steel pipe 18 inches long and 7 inches inside diameter closed at the top and bottom by caps. A gasket of asbestos cloth with wire insertion was used to make the joints withstand a pressure of 350 pounds per square inch. The pressure was indicated on a Fairbanks steam gauge.

3. HYDRATION OF MONOCALCIUM ALUMINATE WITH WATER

The monocalcium aluminate prepared consisted of irregular crystals which sometimes tended toward prismatic development. These were often irregularly intergrown, but twinning, described as a characteristic feature, was not observed. Indices of refraction were $\alpha = 1.642 \pm 0.003$, $\beta = 1.654 \pm 0.003$ and $\gamma = 1.660 \pm 0.003$. The measured double refraction gave $\gamma - \alpha = 0.018 \pm 0.003$. The maximum interference color observed was yellow of the second order. Biaxial interference figures were observed with a fairly small optic axial angle. No grains were found suitable for the quantitative determination of this angle. The optical character was negative. The chemical analysis showed:

	Per cent.
SiO_2	0.46
Al_2O_3	64.31
Fe_2O_3	.16
CaO	34.94
Ignition loss	.15

(*A*) *Hydration on Slide* (*See Table 1*).—The monocalcium aluminate started to hydrate almost immediately. A transparent, amorphous mass first formed around the grains. Then radial spherulites and finally hexagonal plates and needles began to develop, both at the grains and away from them. These continued to grow and attained their maximum size in a few days,

and at the same time the amorphous material covered practically the whole slide. (See Fig. 3a, 3b.) The plates, needles, and spherulites were identical optically and chemically. They exhibited a medium double refraction and were uniaxial positive. The refractive indices were as follows: $\mu_e = 1.552 \pm 0.003$, $\mu_e = 1.535 \pm 0.003$. The character of the principal zone was positive. The needles were plates turned on edge, hence orientated parallel to the crystallographic "c" axis. The spherulites consisted of the needle crystals radiating from a common center.

A slide dried in an atmosphere free from carbon dioxide and tested for free lime and lime hydrate with White's reagent [6] gave a negative result. Another slide, dried as above, was treated with an alcoholic solution of anthrapurpurine which according to Keisermann,[7] dyes only free and combined lime. The needles, plates, and spherulites were dyed red, but the amorphous material was unchanged, showing that the latter contained no lime. Patent Blue, which, according to Keisermann, stains free and combined alumina, stained all the hydration products.

(*B*) *Hydration in Steam at Atmospheric Pressure.*—A 1-gram sample of monocalcium aluminate was placed in the can and rotated while the temperature was raised about 10° above that desired. Then steam was passed through the cylinder and temperature observations were made at frequent intervals. At the conclusion the steam was swept out by a current of natural gas, the cylinder was opened, and the contents were removed. The sample was dried for two hours on a steam plate at 100° in a current of air free from carbon dioxide. Operating in this manner it was possible to prevent the material from absorbing more than slight traces of carbon dioxide. Separate samples were used for each test. The amounts of water absorbed under the above conditions are given below and shown diagrammatically in Fig. 4.

	105°	110°	115°	120°
	Per cent	*Per cent*	*Per cent*	*Per cent*
1 hour	12.00	2.00	0.5	Nil.
2 hours	16.00	4.99	1.3	0.10
4 hours	19.21	6.00	2.1	.15

[6] J. Ind. Eng. Chem., 1, p. 5; 1909.

[7] Cement Eng. News, 23, p. 10; January, 1911.

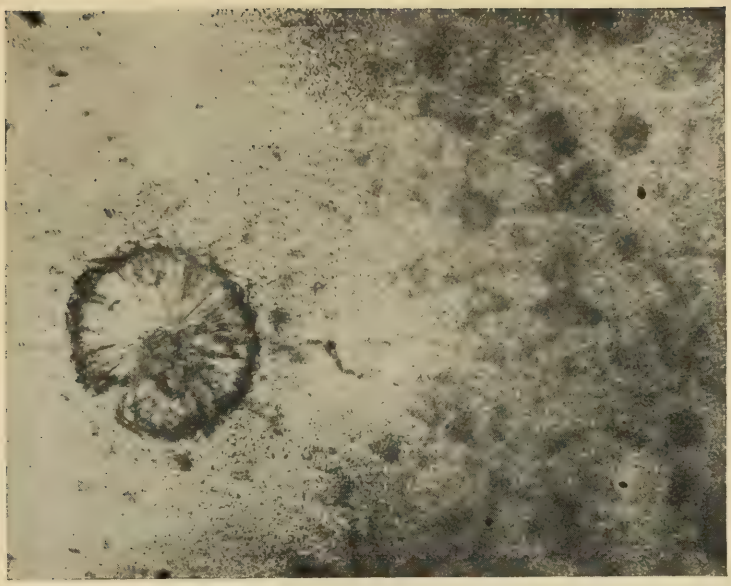

FIG. 3a.—*Monocalcium aluminate in water taken without nicols and showing a large spherulite of hydrated tricalcium aluminate and amorphous hydrated alumina. The latter covers and obscures crystals of hydrated tricalcium aluminate. Magnification = 165 diameters*

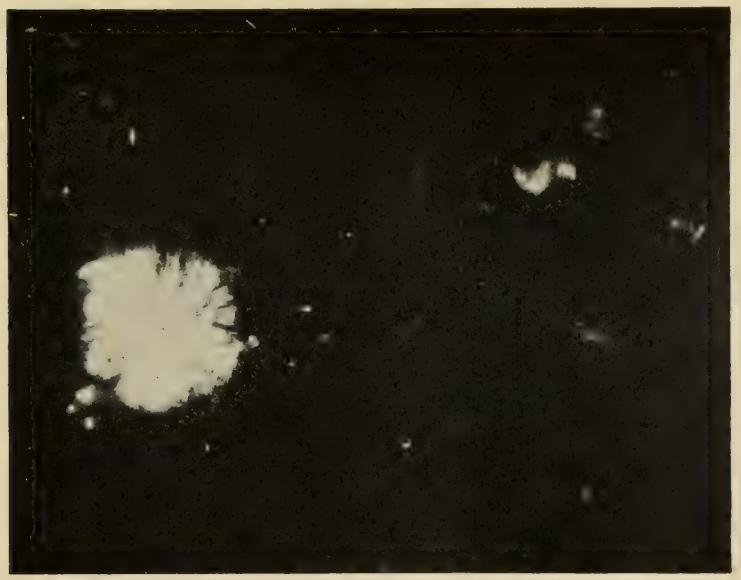

FIG. 3b.—*This photograph is identical with figure 3a except that it was taken with crossed nicols. The amorphous material is invisible, but the crystals covered by it are clearly shown*

The water absorption was greater at 105° than at any other temperature and confirms Bied's statement that the weakly basic aluminates do not absorb water appreciably above 110°. Hydration was not in any case complete, since the microscope showed unhydrated grains surrounded by and coated with a translucent mass of isotropic amorphous material and very fine needles. (The term amorphous and noncrystalline are used to designate any substance which shows no crystallization and is optically isotropic. This would include the colloidal material noted by previous investigators. It was thought best to avoid the use of the words colloid and colloidal material on account of the hazy and contradictory views concerning them set forth particularly by cement investigators.) With increase in duration of exposure up to four hours the needle crystals increased in number and size. The maximum interference color was yellow of the first order, and the crystals showed uniaxial interference figures. These crystals were identical with the needles observed on the slide and were identified as hydrated tricalcium aluminate (see hydration of tricalcium aluminate), indicating that amorphous alumina is split off and hydrated tricalcium aluminate is formed. With increase in temperature up to 140° more of the unhydrated monocalcium aluminate and less of the amorphous material was present. A sample of the material hydrated for four hours at 105° was heated for one hour in air to 160°, when the water content fell to 0.2 per cent and the fine needle crystals disappeared, though the isotropic material was still present.

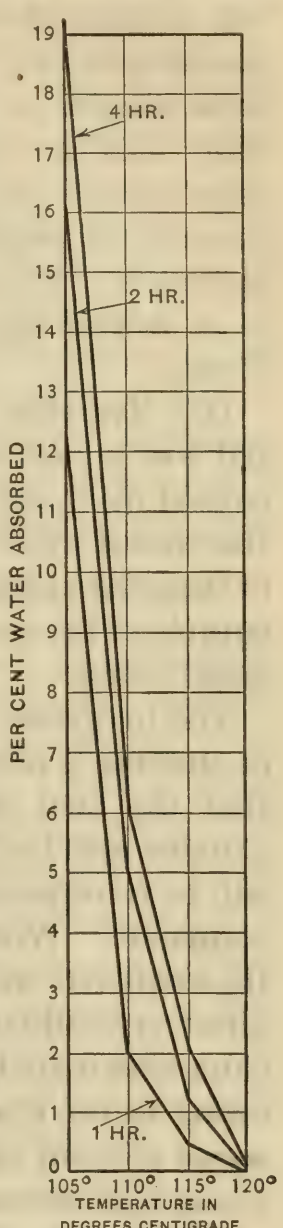

FIG. 4.—*Showing the hydration of monocalcium aluminate in steam*

(*C*) *Hydration in the Autoclave.*—A sample of the aluminate was stirred with a large excess of water in a porcelain crucible. This was covered, placed in the autoclave, and exposed to steam at 300 pounds pressure for two hours. After drying the specimen in the same manner as previously described it was examined microscopically and showed complete hydration with the formation of a large amount of the amorphous material and a very considerable quantity of needles and hexagonal plates of hydrated tricalcium aluminate. It is of significance that complete hydration occurred in so short a time and that considerable crystalline material was formed.

(*D*) *Hydration of Molded Specimens.*—Another sample of material was mixed with 30 per cent of water, pressed into a ½-inch cubical mold, and allowed to hydrate for 24 hours. At the end of this time it was very hard, being more difficult to powder than any of the other aluminates treated the same way. It consisted almost entirely of the amorphous material with a few of the needle crystals noted above.

The hydration of the monocalcium aluminate with splitting off of alumina is noted both by Schott [8] and Keisermann.[9] The fact that the final products of hydration are amorphous hydrated alumina and hydrated tricalcium aluminate is of importance and will be considered further under the discussion of calcium sulphoaluminate. Whether the hydrated tricalcium aluminate forms by the solution of monocalcium aluminate, splitting off of alumina and direct crystallization or from the conversion of amorphous tricalcium aluminate into crystalline material could not be determined, owing to the character of the material. The evidence, however, seems to point to the slow conversion of the amorphous aluminate which is of indeterminate composition into the crystalline variety some time after the hydrated alumina is split off. This latter view will be greatly strengthened when cements hydrated 7 and 28 days are considered. Stern [10] calls attention to the fact that calcium aluminates are decomposed by water, forming calcium hydrate and gelatinous alumina, and if an aluminate is shaken with water

[8] Cement Eng. News, 22, p. 515; 1910.
[9] Cement Eng. News, 23, p. 10; January, 1911.
[10] Chem. Ztg., 32, pp. 1029–1031; 1908.

and filtered both lime and alumina are contained in the filtrate. If this filtrate be dialyzed, lime passes through the dialyzer generally without any alumina, although a trace of alumina may also pass through. The experiment of Stern was repeated (see page 18), but his results were not corroborated. Moreover, the aluminate was carefully tested by White's test [11] in all stages of the hydration, and at no time was the presence of calcium hydrate detected.

In this connection mention might be made of the recent work of Blum [12] on the constitution of aluminates. He studied the *H* ion concentration and electrical conductivity during the reaction of an aluminum salt with an alkali hydroxide. The results of this work add to the evidence in favor of the existence of definite aluminates in the solutions obtained by dissolving aluminum hydroxide in alkalies. This work is very interesting in view of the chemical similarity between the alkalies and the alkali earths.

4. HYDRATION OF 5:3 CALCIUM ALUMINATE WITH WATER

This aluminate was prepared in the usual way by mixing the materials in the proper proportion with a little water, molding into hollow cylinders, and burning them in the updraft kiln.

The sample, as prepared, consisted of irregular isotropic grains with a refractive index of about 1.61. Some of the crystals contained a few inclusions of double-refracting material with a higher index. The optical proportion of this material indicated that it was a mixture of monocalcium aluminate and the compound $2CaO.SiO_2.Al_2O_3$ [13]. These crystals were prominent because of their marked difference from the large mass of isotropic crystals. The amount of these impurities was, however, very small, and their presence doubtless had no effect on the results obtained.

The chemical analysis showed:

	Per cent
SiO_2	0.28
Al_2O_3	51.92
Fe_2O_3	.20
CaO	47.59
Ignition loss	.05

[11] J. Ind. Eng. Chem., **1**, p. 5; 1909.
[12] J. Am. Chem. Soc., **35**, p. 1499; October, 1913.
[13] J. Ind. Eng. Chem., **3**, No. 4, p. 40; April, 1911.

(*A*) *Hydration on Slide.*—The 5:3 calcium aluminate (see Figs. 5a and 5b) began to hydrate almost immediately, the first effect being the formation of an amorphous material around the grains and of spherulites away from the grains. The latter grew in size, and needles and plates, identical with those noted in the hydration of monocalcium aluminate, began to extend from them. These continued to increase in size and reached the maximum development after a few days. The amorphous material also increased in quantity, but the maximum amount was considerably less than that of the hydrated monocalcium aluminate. The amount of crystallized material, however, was much greater.

A slide of hydrated 5:3 calcium aluminate dehydrated in air free from carbon dioxide and treated with White's solution gave negative results. Another slide was similarly prepared. Part of it stained with anthrapurpurine showed absence of lime in the amorphous material, whereas the other portion stained with patent blue showed the presence of alumina in all the hydration products.

(*B*) *Hydration in Steam at Atmospheric Pressure.*—The quantities of water absorbed are given below and represented diagrammatically in Fig. 6:

	105°	110°	125°	140°
	Per cent	*Per cent*	*Per cent*	*Per cent*
1 hour	11.08	8.21	3.10	0.27
2 hours	11.67	9.04	3.75	.34
4 hours	12.62	10.01	4.20	.39

At 105° a considerable amount of the material was changed and was coated with amorphous material and doubly refracting uniaxial needles. As the temperature increased the amount of amorphous material decreased, until at 140° there was extremely little of it present, and at 150° nothing but unchanged 5:3 aluminate was observed.

The silicate noted in this preparation of aluminate in all cases was unaffected by the steam treatment. The maximum water absorption occurred at 105°, but the amount was less than the corresponding absorption of the monocalcium aluminate. How-

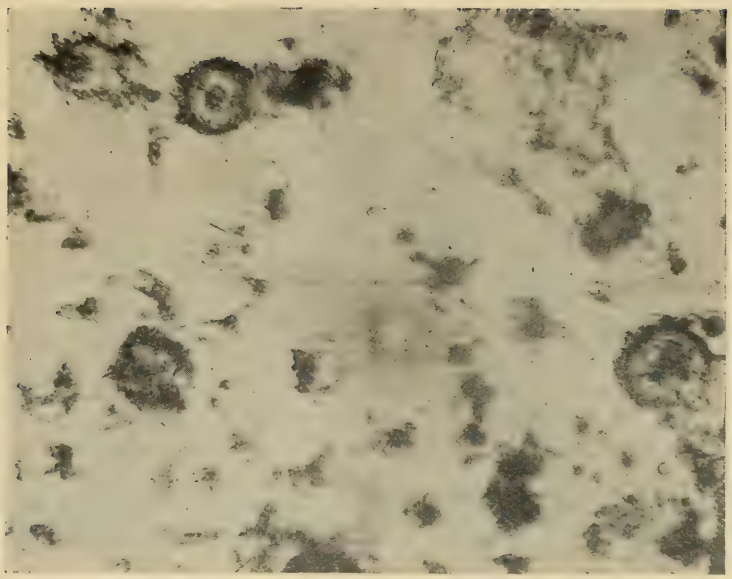

FIG. 5a.—*5:3 calcium aluminate in water, showing needles, plates, and spherulites of hydrated tricalcium aluminate and amorphous hydrated alumina. This photograph was taken without nicols. Magnification = 180 diameters*

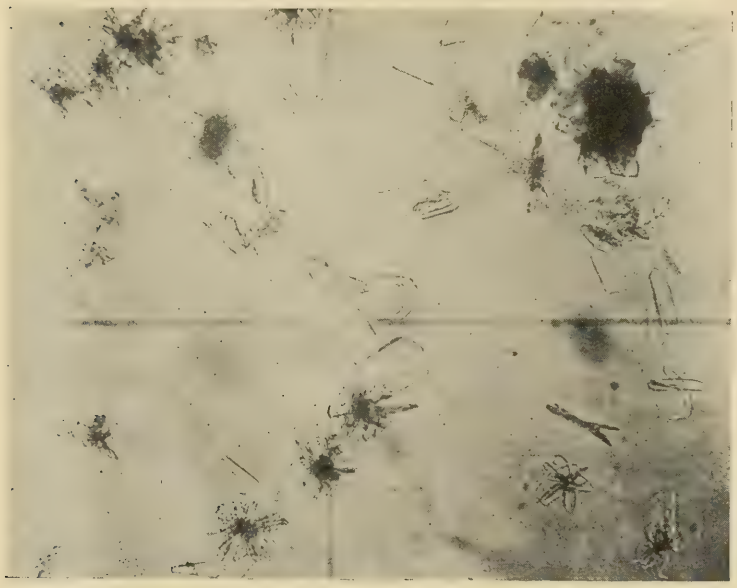

FIG. 5b.—*5:3 calcium aluminate in water, showing needles and plates of hydrated tricalcium aluminate and amorphous hydrated alumina; taken without nicols. Magnification = 300 diameters*

ever, the increase in lime content seems to allow the absorption of water at higher temperatures. The material hydrated at 110° was reheated to 160° in steam, and it was found that the needle crystals were destroyed.

(*C*) *Hydration in the Autoclave.*—For this test a sample of the material was stirred with water in a small porcelain crucible, covered and heated at 300 pounds for two hours in the autoclave. The results showed complete hydration with the formation of lath-shaped prismatic crystals, small hexagonal plate crystals, and a small amount of amorphous material. The optical properties of the crystals established them as hydrated tricalcium aluminate.

(*D*) *Hydration of Molded Specimens.*—Molding of specimens with 28 per cent of water showed after 24 hours very little development of crystals and much amorphous material. Variations in the water content thus simply cause varying amounts of crystalline material to be formed immediately on hydration, the resulting products in each case being identical.

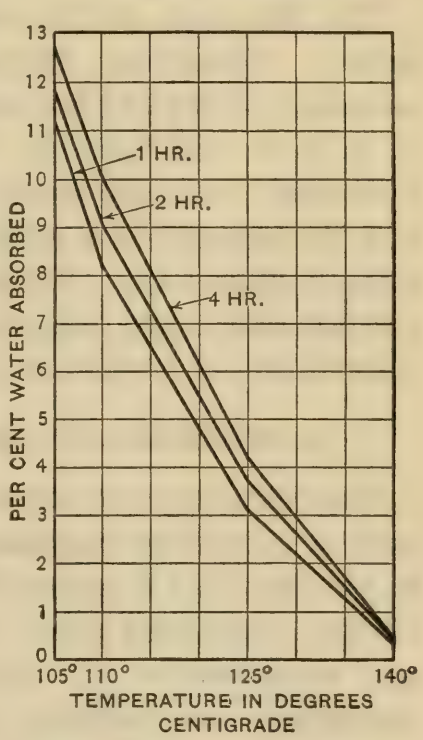

FIG. 6.—*Showing the hydration of 5:3 calcium aluminate in steam*

One further fact concerning the hydration of 5:3 calcium aluminate is worthy of emphasis, namely, that the microscopical examination of the hydrated product revealed no free lime or lime hydrate, but that hydrated tricalcium aluminate was found in all cases. Cements usually contain some free lime and sometimes 5:3 calcium aluminate. Under these conditions it is probable that quantities of the hydrated aluminate would be formed by combination of calcium hydrate and the hydrated alumina split off from the 5:3 calcium aluminate, although such a process would seem to be a slow one. Kasai[14] found that on addition of hydrated silica and alumina to cement only the former was of value. Yet the

[14] Ciment, **17**, pp. 41–44, 61–63; 1912.

action of the hydrated alumina, split off in the presence of calcium hydrate, can not be predicted from the combination of calcium hydrate and precipitated, washed alumina, as the two materials would differ materially in their behavior, owing to their different methods of formation. Gallo [15] has already called attention to the formation, in puzzalona mortars, of a compound of the formula $3CaO.Al_2O_3.10H_2O$ from soluble calcium aluminate in the presence of calcium hydrate.

The literature on the subject of the 5:3 calcium aluminate is scanty. Excepting Michaelis, who states that 5:3 calcium aluminate is present in cement, the only noteworthy mention made of it is in the work of the Geophysical Laboratory. Various hydration tests are found on the so-called dicalcium aluminate, but this usually is a mixture of 5:3 calcium aluminate and tricalcium aluminate. Where the product is fused, it consists of 5:3 calcium aluminate, tricalcium aluminate, and free lime, due to the dissociation of tricalcium aluminate.

5. HYDRATION OF TRICALCIUM ALUMINATE WITH WATER

More difficulty was experienced in securing a homogeneous specimen of tricalcium aluminate than of the other aluminates, owing to the fact that it was underburned at first, forming a soft porous clinker containing much free lime, a little tricalcium aluminate, and considerable 5:3 calcium aluminate. On pulverizing and regrinding and burning part of it fused. The microscopical examination of the fused product revealed the same constituents as in the underburned specimen, the only difference noted being a growth in size of the free lime grains. A third pulverization and burning resulted in a satisfactory specimen. It was found necessary, however, to hold the temperature at least 50° below the fusion point in order to secure the best results. The material yielded on analysis:

	Per cent.
SiO_2	0.48
Al_2O_3	37.78
Fe_2O_3	.16
CaO	61.41
Ignition loss	.23

[15] Gazz. Chim. Ital., 38, II, pp. 156–204; 1908.

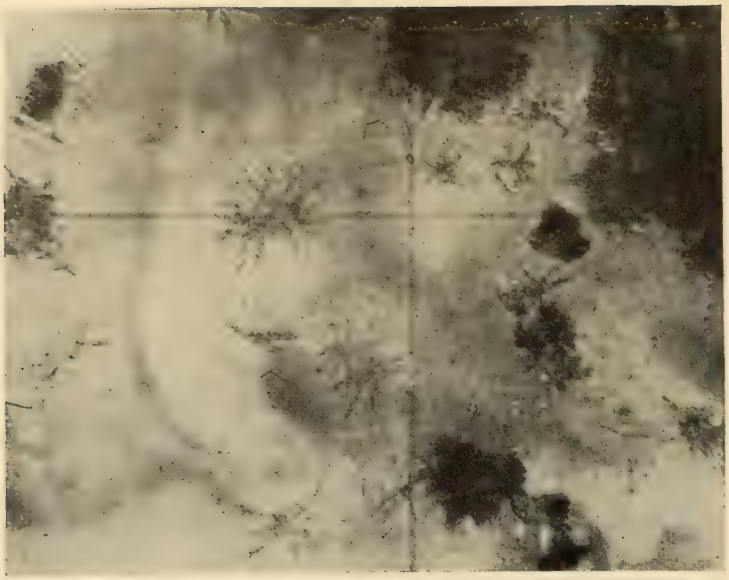

FIG. 7a.—*Tricalcium aluminate in water, showing hexagonal plates, needles, and needle aggregates of hydrated tricalcium aluminate; taken without nicols. Note the absence of amorphous, hydrated alumina. Magnification = 250 diameters*

FIG. 7b.—*This photograph is identical with figure 7a except that it was taken with crossed nicols. Note the crystallinity of the apparently amorphous aggregates*

It consisted almost entirely of irregular to cubical isotropic grains, with the refractive index equal to 1.710. No definite cleavage was observed.

(*A*) *Hydration on Slide.*—Almost immediately fine needles and small hexagonal plates were formed at and away from the tricalcium aluminate grains (see figs. 7a and 7b). These were very minute at first, but grew in size and reached maximum growth at the end of a few days. The determination of their optical properties proved them to be identical with each other and also with the needles and plates observed in the hydration of the other aluminates. The plates were orientated perpendicular to the "C" crystallographic axis and the needles were orientated parallel to this axis. No amorphous hydration product was observed, this being in contradistinction to the observations with 5:3 calcium aluminate and monocalcium aluminate. A slide of hydrated tricalcium aluminate dried in an atmosphere free from carbon dioxide and treated with White's reagent, gave negative results. The absence of lime hydrate and amorphous hydrated alumina establishes the composition of this compound as hydrated tricalcium aluminate.

(*B*) *Hydration in Steam at Atmospheric Pressure.*—On exposure for four hours at 110° only a little tricalcium aluminate was hydrated. Some of the grains showed a border of doubly refracting material consisting of fairly well-developed needles and some plates of hydrated tricalcium aluminate, together with some amorphous material. Increasing the temperature to 140° served merely to lessen and prevent the formation of the crystals. The formation of the border of hydrated crystalline and noncrystalline material seems to indicate that the trialuminate goes first through an amorphous condition previous to crystallization. The amount of water absorbed by the three aluminates decreases as the lime content increases, and the large water absorption of monocalcium aluminate and 5:3 calcium aluminate is due to taking up of water by the amorphous hydrated alumina which is split off. White's test in every case failed to show the presence of calcium hydrate, so that again there was no evidence in favor of dissociation into calcium hydrate and hydrated alumina. The two reactions involved are simply the addition of water with formation of an

amorphous, hydrated aluminate, and the subsequent crystallization of this compound. Under the special conditions obtaining when tricalcium aluminate is hydrated on a slide with a large excess of water, the amorphous condition is either of very short duration, or else it is entirely lacking, and the material hydrates immediately as crystals of hydrated tricalcium aluminate. The

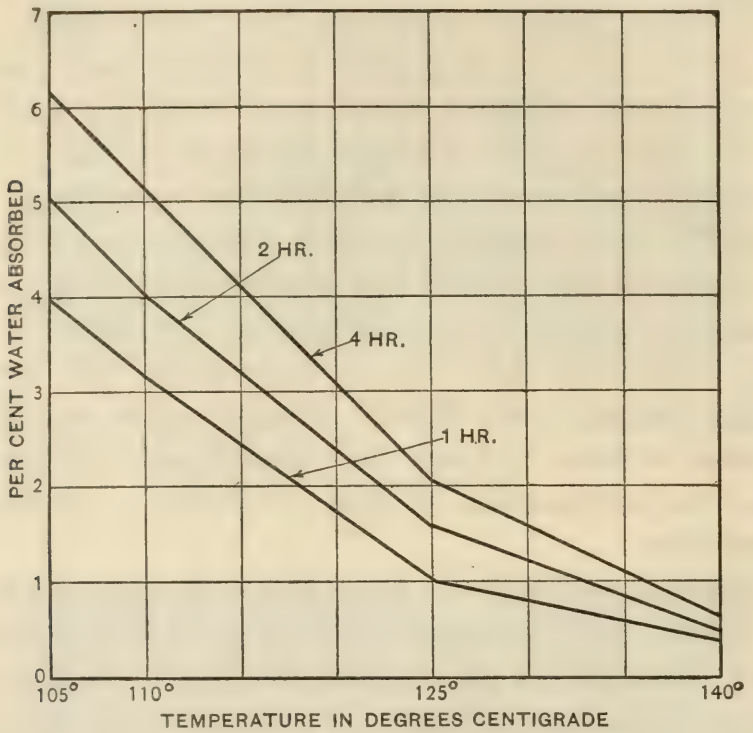

FIG. 8.—*Showing the hydration of tricalcium aluminate in steam*

quantities of water absorbed are given below and shown diagrammatically in Fig. 8:

	105°	110°	125°	140°
	Per cent	Per cent	Per cent	Per cent
1 hour	3.99	3.19	1.02	0.37
2 hours	5.01	4.10	1.56	.49
4 hours	6.21	5.19	2.12	.65

(*C*) *Hydration in Autoclave.*—A sample of tricalcium aluminate was stirred with an excess of water in a porcelain crucible and heated in an autoclave for two hours at 300 pounds pressure.

The microscopic examination showed that all the material had hydrated. The hydration product was chiefly amorphous but contained a few hexagonal plates as well as needles. Test of the amorphous material with anthrapurpurine and patent blue proved it to be hydrated tricalcium aluminate. There was an increase in the amount of crystals over those noted in the steamer.

(*D*) *Hydration of Molded Specimens.*—Mixing the material with 30 per cent of water and molding it caused the liberation of much heat and quick setting of the material, which became granular and very difficult to trowel. Examination after 24 hours showed that but a small portion of the material had hydrated. Only the edges of the grains were changed to the usual amorphous condition. The liberation of heat is interesting in view of the apparent endothermic reaction taking place when it is subjected to steam at atmospheric pressure. No explanation of this difference is made.

(*E*) *Composition of the Hydrated Tricalcium Aluminate.*—In an effort to determine the composition of the hydrated aluminate a 2-gram sample was shaken in a jar completely filled with 150 cc of boiled distilled water, the material being examined from time to time to determine when crystallization was complete. The addition of water resulted in the formation of lumpy, amorphous, hydrated aluminate on the outside of the grains, which had a tendency to cohere and prevent the penetration of more water. These lumps were broken up by shaking the suspension with steel shot, and in eight days all the amorphous material had been converted into fine crystals of hydrated tricalcium aluminate. The material was dried for two hours on a steam plate at 100° and the analysis gave:

	Per cent	Molecules
Al_2O_3	27.52	1.0
CaO	45.60	3.0
H_2O	26.94	5.5

This corresponds to the formula of $3CaO.Al_2O_3.5\,1/2H_2O$. Another portion of the material was dried in a vacuum dessicator over sulphuric acid for 48 hours, and had the composition of 3CaO.

$Al_2O_3.9H_2O$. The water content as determined should be considered more or less approximate, since the vapor-pressure method must be used when the highest degree of accuracy is required.

6. DIALYSIS EXPERIMENT

In an effort to ascertain whether with actual solution in a large excess of water the aluminates are hydrolyzed into calcium and aluminum hydrates, Stern's[16] experiment was repeated. The apparatus, a diagram of which is given in Fig. 9, consisted of a two-hole bell jar (A) on a glass plate (B) with a ground contact

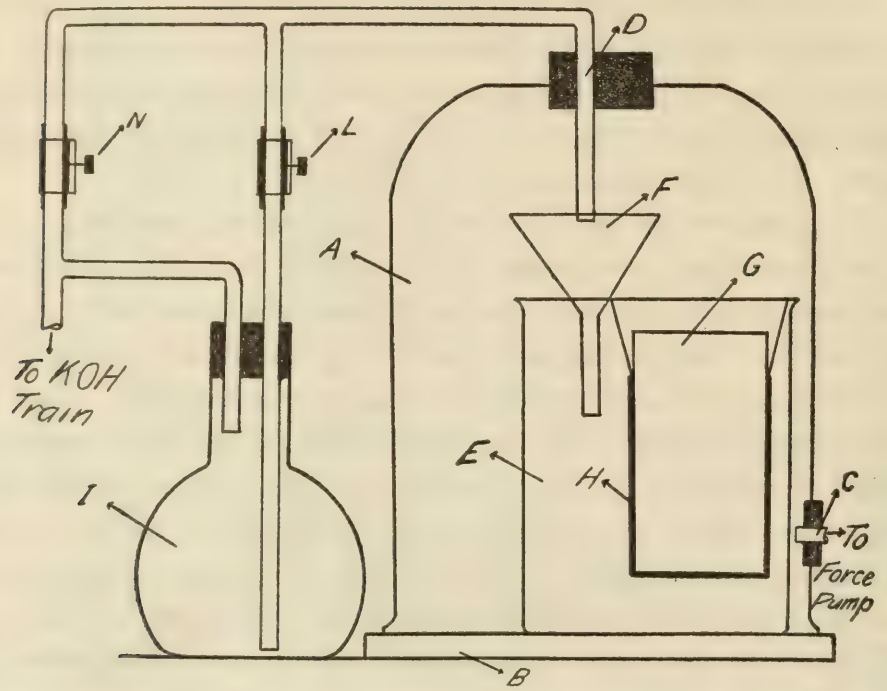

FIG. 9.—*Showing filtering and dialysing apparatus*

which was made air-tight. Connections were made at (C) with a vacuum pump and at (D) with the flask (I) and the potash train. Inside the jar was placed a beaker (E) containing, suspended, a funnel (F) and a piece of wide glass tubing (G), around one end of which was stretched a parchment paper (H) as dialyzing membrane. The parchment was examined carefully with a hand glass and microscope for flaws. A little tricalcium aluminate was mixed with a large excess of water in the flask (I), and the flask was shaken at intervals for ten days until a saturated solution had

[16] Chem. Ztg., 32, pp. 1029–1031; 1908.

been formed. Care was taken to exclude carbon dioxide, owing to its great affinity for hydrated aluminates; but with all precautions some calcium carbonate was formed, and it was necessary to filter this together with the solid hydrated tricalcium aluminate before dialysis could be carried out. To avoid any further carbonation, it was necessary first to remove all carbon dioxide from the bell jar containing the beaker (H) and then to filter the solution into the beaker. This was accomplished in the following manner:

The necessary amount of distilled water free from carbon dioxide was placed into the dialyzing tube (G), the bell jar (A) was hermetically sealed on plate (B), and at (D) connection was made with the potash train by closing the cock (L). The cock (N) was closed, and by means of the vacuum pump the bell jar was evacuated. Then the cock on the force-pump line (not shown in diagram) was closed, and (N) was opened sufficiently to allow a steady stream of air free from carbon dioxide to enter the bell jar. This operation was repeated five times. Connection was then made through the flask by closing (N). By regulating the force pump and the cock (L) the contents of the flask was siphoned drop by drop through the filter (F) and into the beaker (E), the operation being carried out in an atmosphere entirely free from carbon dioxide.

The apparatus was allowed to stand for 11 days before the contents of the dialyzing tube (G) was analyzed. Contrary to Stern's statement, both lime and alumina were found, and in the proportion of almost 3 to 1. This tends to show that the lime and alumina, which passed through the parchment, did so as the hydrated tricalcium aluminate and that there was no hydrolytic dissociation.

7. HYDRATION OF TRICALCIUM ALUMINATE CONTAINING 5:3 CALCIUM ALUMINATE AND FREE LIME, WITH WATER

As free lime has been found by microscopic investigation to be a usual constituent of high limed cements, a sample of material, containing about 20 per cent less alumina than that required to form the tricalcium aluminate, was burned and then examined petrographically. The major portion of the material consisted of tricalcium aluminate, but a considerable amount of high-

burned free lime and a minute quantity of 5:3 calcium aluminate were also noted.

(*A*) *Hydration in Steam at Atmospheric Pressure.*—The most marked temperature variations of all the specimens were noted here. For instance, in hydrating a sample at 110°, it was noted that for 20 minutes after the beginning of the operation the inner thermometer showed 110-111° and the outer 118°. At the end of this period the inner temperature suddenly fell to 101°, and it became necessary to bring the outside temperature to 190° before the inner temperature rose to the required point. It was found

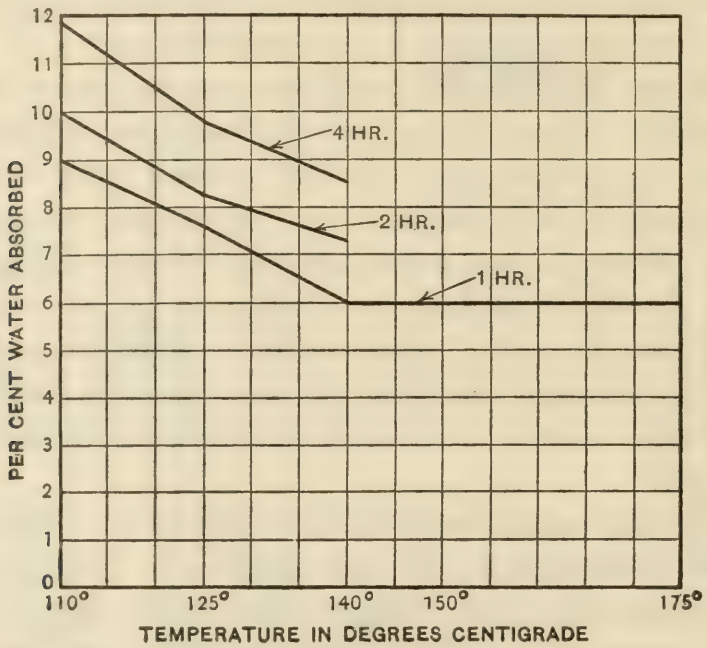

FIG. 10.—*Showing the hydration of tricalcium aluminate, 5:3 calcium aluminate and lime in steam*

necessary to hold the outer temperature at 190° during the rest of the period, because of this strong endothermic reaction. The hydration of this mixture of compounds at 110° for one hour showed a little unhydrated lime, amorphous lime hydrate, but no crystalline hydrate, and a small amount of hydrated tricalcium aluminate. With increase in time much larger amounts of material were hydrated, though even at the end of four hours not all the lime had been converted into hydrate. With increase in temperature the amount of hydrated material decreased. However, the lime did not cease hydrating at 175°, the limit of the test.

The quantities of water absorbed are given below and shown diagrammatically in Fig. 10.

	110°	125°	140°	150°	175°
	Per cent	Per cent	Per cent	Per cent	Per cent
1 hour	8.90	7.60	6.04	6.03	6.00
2 hours	9.91	8.29	7.20	.....	.....
4 hours	11.85	9.76	8.54	.....	.....

The curve of the percentage water absorption is nearly a straight line for higher temperatures, showing that the free lime was still being hydrated.

(*B*) *Hydration on Slide.*—Hydrated with excess of water on the slide the specimen showed crystallized hydrated tricalcium aluminate and amorphous material, some of which gave the characteristic lime phenolate crystals with White's reagent.

(*C*) *Hydration in Autoclave.*—A specimen hydrated in the autoclave also gave crystallized hydrated tricalcium aluminate as well as amorphous material. In addition a few incompletely developed crystals of calcium hydrate were noted.

(*D*) *Hydration of Molded Specimens.*—A specimen hydrated with 30 per cent water and molded into a cube, showed after 24 hours amorphous calcium hydrate, amorphous hydrated aluminate, and considerable unhydrated material, including free lime.

8. HYDRATION OF LIME

The previous results of the hydration of the aluminate mixed with free lime in steam at atmospheric pressure show that with steam acting on material passing through the 200-mesh sieve no crystalline calcium hydroxide is formed while in the autoclave with the same material hexagonal plates of hydrate are found, indicating that with increased heat and increased pressure lime is taken into solution and crystallized out. To determine whether the presence of an excess of water was responsible for this phenomena, a number of lime samples burned at various temperatures from 1200 to 1400° for one hour were exposed on slides after preliminary sifting. The sample burned at 1400° and passing the 200-mesh sieve after 48 hours hydration on the slide consisted

mainly of amorphous hydroxide with a small amount of crystalline material tending toward hexagonal development, showing birefringence but too poorly developed to permit of determination of optical constants. The material retained on the 200-mesh sieve showed considerable crystallized hydroxide in rounded to hexagonal and prismatic crystals, which grew very little in 28 day's time. Lime burned at 1300 to 1400° C—in other words, at temperatures approximating cement kiln usage—is referred to as high-burned lime. This is in contradistinction to low-burned lime, which is that burned at lime-kiln temperatures (about 1100° C).

The material burned at 1300° and retained on the 200-mesh sieve also showed considerable amounts of crystallized hydroxide, while that burned at 1200° showed mainly amorphous hydroxide with a few grains of doubly refracting material. Furthermore, a slide consisting of a commercial high calcium lime in water showed only amorphous calcium hydroxide. This indicates clearly that the burning temperature and the fineness of grain are controlling factors in determining whether the hydrated product will be amorphous or crystalline. Given the same fineness with decreasing burning temperature, the rate of hydration is increased so that supersaturated solutions are quickly formed and the lime precipitated in the amorphous condition, while as the burning temperature increases the lime goes more slowly into solution and forms a supersaturated solution very slowly, thus permitting crystal growth.

Further tests were made by exposing the lime burned at 1400° to water vapor. The material passing the 200-mesh sieve and that retained on it were placed for seven days on slides over water contained in a jar. At the end of this time the fine material (that passing through the 200-mesh sieve) was quite damp and soft, and consisted almost entirely of amorphous hydroxide with a few grains showing gray to white interference colors. The material retained on the sieve was quite dry, but lost 5.6 per cent on ignition and consisted mainly of small calcium hydrate crystals and a little amorphous material. According to Goldammer [17] the solubility of lime hydrate decreases with rise of temperature, lime

[17] Pharm. Centralle., **26**, p. 442; 1890.

having the power to form supersaturated solutions, while lime hydrate has not. We should therefore expect the hydrate in the autoclave to be unchanged, while the lime, according to its fineness, would yield crystallized or amorphous hydrate. This was found to be true at all temperatures and pressures employed.

Calcium hydroxide crystallizes as short, flaky, tubular hexagonal crystals. Twinning has never been observed, but the crystals sometimes show parallel grouping and skeletal development. Very good cleavage is observed parallel to (0001). Under the microscope they show a clear hexagonal outline when orientated perpendicular to the "c" crystallographic axis, but when resting on edge they exhibit a prismatic to an acicular structure. The double refraction is medium, the interference colors varying considerably with the thickness of the grain and its orientation. Some of the hydroxide crystals are thick enough to show third and fourth order interference colors. The indices of refraction are as follows: $\mu_o = 1.581 \pm 0.002$, $\mu_e = 1.557 \pm 0.002$. $\mu_o - \mu_e$ measured on a grain orientated parallel to "c" axis $= 0.023 \pm 0.003$. The interference figure is uniaxial and the optical character is negative. Lime hydrate resembles hydrated tricalcium aluminate very closely, but is differentiated by the fact that the crystals of the former are invariably larger and have a higher index of refraction. A form of lime hydrate crystallizing in the orthorhombic system has been mentioned by Glinka [18] but this was not observed.

9. ALUMINATES HYDRATED IN CALCIUM HYDROXIDE, $Ca(OH)_2$

In determining the effect of calcium hydroxide on the aluminates, no tests in steam at atmospheric pressure were made because of the poor crystal development obtained by steam on the aluminates alone. Molded specimens of the aluminates were hydrated for various lengths of time and other samples were heated in the autoclave up to 300 pounds. Furthermore, slides were made of the various aluminates hydrating in saturated hydroxide solutions. In every case the resultant products were examined microscopically.

(*A*) *Hydration on Slides.*—The hydration on slides showed the same products as those observed on slides with distilled water.

[18] Bull. Soc. fr. Min. **110**, p. 63; 1887.

Tricalcium aluminate hydrated as such without the formation of amorphous material. 5:3 calcium aluminate split off hydrated alumina and formed needles, plates, and spherulites of hydrated tricalcium aluminate. Monocalcium aluminate acted the same way, but split off more alumina. No new type of crystals which might indicate hydrated tetracalcium aluminate was observed.

(*B*) *Hydration of Molded Specimens.*—A number of specimens were mixed with 30 per cent of water, placed in molds and allowed to harden under a damp cloth for 24 hours. At the end of this time they were removed from the molds and stored for seven days in tightly stoppered bottles, some filled with distilled water, others with limewater. In the specimen of monocalcium a luminate in water the microscopical examination showed much amorphous material, a few grains still unhydrated, and a considerable number of hydrated tricalcium aluminate needles. In the specimen hydrated in limewater, there were more needles observed than in pure water, indicating an action between the hydrated alumina split off and the calcium hydroxide of the solution. Gmelin [19] states that hydrated alumina absorbs calcium hydroxide forming with it an insoluble combination.

The specimen of 5:3 calcium aluminate hydrated in water and in limewater showed no difference in hydration.

The tricalcium aluminate specimens contained fewer needles in both water and hydrate solution than either of the other two aluminates. At the same time their ignition losses were higher. This is due to the fact that at the moment of hydration a dense amorphous material was formed which held its water tenaciously and did not give it up at 100°. The specimen hydrated in limewater contained still unhydrated grains at the end of seven days, and in addition a few small hexagonal plates and needles were found. The same compound kept in water also contained unhydrated grains at the end of seven days.

Another set of specimens was mixed with 5 per cent of dry calcium hydroxide and with 30 per cent of water, stored for 24 hours under a damp cloth and then placed in water and limewater, for 28 days. The monocalcium aluminate specimen showed at the

[19] Handbook of Chemistry, III, p. 327; 1849.

end of this period no unhydrated material, considerable amorphous material and small needles, spherulites, and plates of hydrated tricalcium aluminate, while the specimen hydrated in lime hydrate solution showed a better needle development. The 5:3 calcium aluminate specimens showed no visible difference in the two solutions. No unhydrated material was present. The tricalcium aluminate specimens likewise showed amorphous material, needles, and plates. The period from 7 to 28 days was therefore sufficient to hydrate all the material and cause an increase in the number and size of the hydrated tricalcium aluminate crystals.

According to Le Chatelier [20] and Read,[21] a tetracalcium aluminate was obtained by hydrating cement with limewater, but in no case did the addition of calcium hydroxide in any way change the composition or the character of the crystalline hydration products.

In addition, a 2-gram sample of tricalcium aluminate was shaken for 10 days in a closed flask with calcium hydroxide solution until all the material had been converted from the amorphous to the crystalline state. The suspension was then filtered, washed with alcohol, and dried in a dessicator over sulphuric acid for 24 hours, and the analysis of the residue gave a compound of the formula $3CaO.Al_2O_3.10\frac{1}{2}H_2O$.

(*C*) *Hydration in the Autoclave.*—The various aluminates hydrated with an excess of limewater in the autoclave for two hours at 300 pounds pressure gave products which in no way differed from those obtained in the autoclave with water. The chief distinction noted was in the greater amount of plate crystals formed.

These hexagonal crystals were peculiar in that frequently only three sides of the hexagon were present, the rest of the crystal being irregularly shaped. The aluminates were in every case completely hydrated after two hours, there being no grains present with unhydrated centers and hydrated edges.

In the autoclave the addition of calcium hydroxide in dry powder decidedly retarded the crystal growth of the aluminates. This was particularly noticeable in the specimens of 5:3 calcium aluminate in which, with 1 per cent dry hydroxide, small plates were noted;

[20] J. Soc. Chem. Ind., **3**, pp. 485–486; 1884. [21] Ibid. **29**, p. 735; 1910.

with 10 per cent hydroxide these had disappeared, and with 50 per cent hydroxide only amorphous material was observed. With the trialuminate the effect was manifested in a retarding action on the hydration. With 1 per cent hydroxide, a little unhydrated aluminate and quite a few crystals were noted. With 10 per cent hydroxide considerable unhydrated aluminate was present, together with amorphous hydrate, though a few crystals were observed. With 50 per cent the amount of hydrated material had decreased, and the crystals had almost completely disappeared.[22]

10. ALUMINATES HYDRATED WITH CALCIUM SULPHATE ($CaSO^4$)

With the addition of plaster of Paris ($CaSO_4.1/2H_2O$) to the aluminates all the various hypotheses concerned in the setting of cement become involved. The field is very broad and requires that consideration be given to all the salt solutions used to accelerate and retard setting. Since this investigation deals only with the hydration of cement, the problem is confined to the changes taking place in the aluminates with the addition of plaster, this being an almost universal constituent of Portland cement.

(*A*) *Hydration of Molded Specimens.*—Tests were made by mixing the specimens with calcium sulphate solutions of various known strengths. The first effect noted was the prevention of the evolution of any considerable amount of heat. This was particularly noticeable in the case of tricalcium aluminate, which, on mixing with 25–30 per cent of water, evolved sufficient heat to drive off part of the water as steam. This specimen was particularly examined for the presence of free lime. Its absence showed that the heat evolved was entirely due to the combination of water with the aluminate. Amorphous material was formed which was granular and had little cohesion. With the specimens hydrated in calcium sulphate solution the amorphous material was still formed, but at a slower rate, and the heat evolution was much lessened. To determine the effect of calcium sulphate solution on the extent of hydration, a number of samples were mixed with 30 per cent calcium sulphate solutions of known strengths. These were allowed to harden for 24 hours, then stored in water for 6

[22] Ninth Ann. Trans. Nat. Assoc. Lime Mnfrs., pp. 16–25; 1911.

days, and dried for 2 hours at 100°. The ignition losses were as follows:

Strength of calcium sulphate solution	0.01 per cent	0.05 per cent	0.1 per cent	Saturated solution
	Per cent	Per cent	Per cent	Per cent
Monocalcium aluminate	29.20	28.90	28.18	30.12
5:3 calcium aluminate	27.38	27.86	26.78	28.84
Tricalcium aluminate	24.50	25.06	23.06	27.28

It is noticeable that the 0.1 per cent solution gave the lowest results in each case, and this effect will be referred to later in connection with setting time. The saturated solutions gave the highest ignition losses. It is believed that the slower rate of hydration which occurs with the saturated solution permits greater penetration of water toward the center of each grain. Microscopic observations have shown that hydration takes place first around the edges of each grain and slowly proceeds toward the center. Thus in the case of the aluminates, containing no plaster, the amorphous gelatinous mass is formed instantly around each grain, preventing the ready penetration of water. Plaster, therefore, tends to keep the pores of amorphous material open.

It is very interesting to note that with monocalcium aluminate, after seven days' hydration, only that specimen hydrated in saturated calcium sulphate solution showed complete hydration, while those hydrated in weaker solutions showed unhydrated cores surrounded by hydrated material. In the case of 5:3 calcium aluminate at the end of seven days there was still a small amount of unhydrated material. The saturated calcium sulphate solution, however, gave the best crystal development. With tricalcium aluminate the above was likewise true, both amorphous and crystalline hydrated tricalcium aluminate being present. The reason for the presence of unhydrated material in the last two aluminates and not in monocalcium aluminate is due to the fact that amorphous hydrated alumina is present in the monocalcium aluminate specimens, a less amount in 5:3 calcium aluminate, and none in the tricalcium aluminate. This material coagulates very slowly, allowing a ready penetration of water, and, therefore, a correspond-

ing greater hydration. At the same time it dries out to a hard dense mass, the monocalcium aluminate giving very strong specimens as compared with the other two. In all the above specimens minute crystallites of a new compound, calcium sulphoaluminate, were noted.

(*B*) *Theories Concerning Retardation of Initial Set by the Use of Plaster.*—The effect of variation in the per cent of plaster above

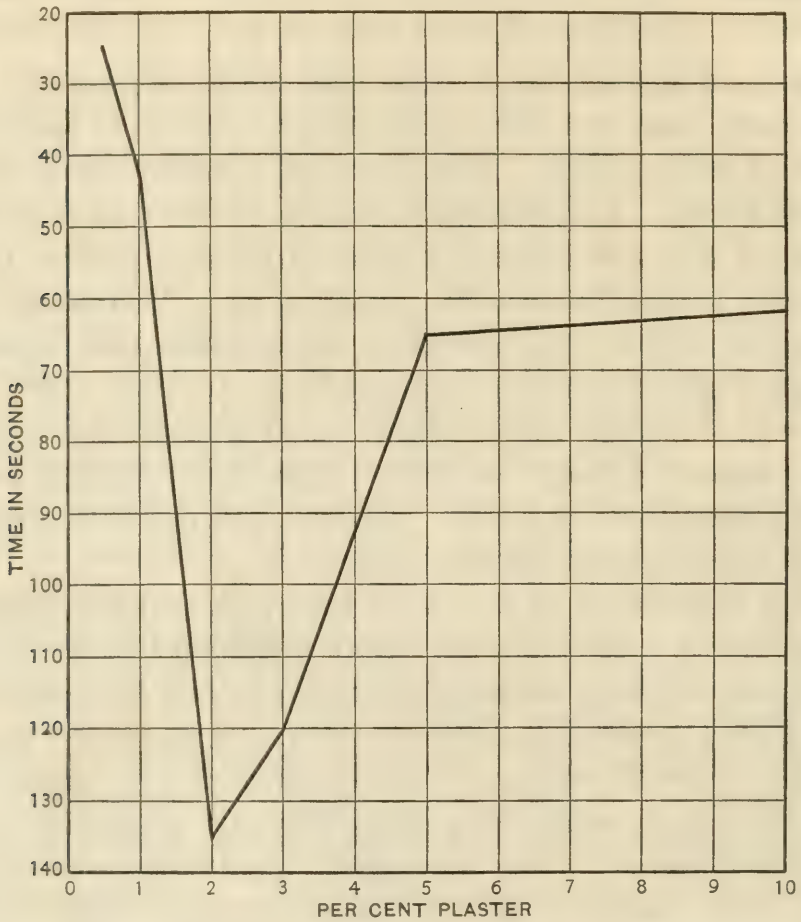

FIG. 11.—*Showing the per cent plaster—time of set curve for tricalcium aluminate*

or below a certain definite concentration, causing a decrease in the setting time, has been noted by Rohland [23] and other observers.

The fact that a minimum and a maximum concentration of calcium sulphate gives a rapid set and an intermediate concentration a slow set (see Fig. 11) seems to disprove Reibling's theory [24] that as plaster dissolves, it ionizes and reduces the solubility of other

[23] Stahl und Eisen, 28, pp. 1815–1819; 1908. [24] Philippine J. Science, 6 (3), p. 210; 1911.

calcium ions already present, causing free lime to be less rapidly dissolved, the hydration of the aluminate to take place more slowly, and the setting to be retarded. If this were the case, then increasing amounts of plaster should give a correspondingly slower set, on account of the continued decrease in the solution of other lime ions already present.

The sulphoaluminate theory does not suffice to explain the retardation of the setting of cements. In observing the behavior of the above specimens under the microscope, no selective action with the water present could be noted. The aluminate began at once to hydrate, and at the same time sulphoaluminate needles were formed, their quantity steadily increasing from the beginning to the end of the initial set. However, their number at any time was very small, and, increasing the amount of plaster, though increasing the amount of sulphoaluminate needles, did not retard the set. Furthermore, the formation of sulphoaluminate needles is not sufficient to account for the retarding action of salts, such as calcium chloride, sodium borate, potassium bichromate, sugar, or other carbohydrates, which, so far as is known, do not form insoluble compounds with aluminates at the concentration used.

The problem of the retardation of the setting of cement appears to be one involving the action of electrolytes carrying positive or negative charges. This field has been investigated by colloid chemists and is treated in a general way by authors on colloid chemistry, i. e., Freundlich,[25] Ostwald,[26] Pöschl,[27] etc. Rohland[28] has attempted to apply the general principles to the particular case of Portland cement. Although the action of electrolytes offers the best explanation so far found, nothing has been definitely proven, and much more work must be done on the problem.

In referring to setting as a problem dealing with the action of electrolytes, there seems to be an analogy with the results obtained by the Ceramic Division of the Bureau in using the process for

[25] Kapillarchemie, 1909; Die Einwirkung der Elektrolyte auf Suspensionkolloide, pp. 345–364; Einfluss der Elektrolyte auf grobe Suspensionen, pp. 365–368.

[26] Grundriss der Kolloidchemie, pp. 467–505; 1910.

[27] The Chemistry of Colloids, pp. 14–17; 1910.

[28] Zs. Angew. Chem., **16**, pp. 1049–1055, 1903; Tonind. Ztg., **28**, p. 77, 1904; Chem. Ztg., **30**, pp. 1173–1174, 1906; Zs. Chem. Ind. Kolloide, **8**, pp. 251–253, 1911.

thinning clay slips by means of electrolytes. In this process extremely small quantities of an electrolyte are added to a clay slip. At definite concentrations of electrolytes in the slip there are points of maximum and minimum viscosity. At the point of minimum viscosity the less finely dispersed matter settles out fairly rapidly, while the finely divided material stays in suspension. By increasing or decreasing the concentration of electrolytes complete coagulation results. The curve is of the same general nature as that shown for the per cent of plaster-time curve for tricalcium aluminate. It is evident here that with 2 per cent plaster the amorphous material formed by the addition of water can least readily coagulate and separate as a solid from the semiliquid mass, while at another concentration of plaster the conditions for coagulation are more favorable and the separation of a solid mass occurs in a shorter time.

McKenna [29] has called attention to the fact that the amorphous material separates in at least two stages, normal cements showing at about the third hour a relaxation of the first stiffening, followed by a resumption of the hardening. The explanation given is that the break indicates the separation of a compound from supersaturated solution and softening of the amorphous mass by the freed water. Later by absorption of water hardening proceeds. Bleininger [30] likewise states that the conductivity of a paste of cement and water increases enormously at the time of initial set, which is in favor of a supersaturation theory.

The evidence, therefore, is in favor of the fact that the aluminates coagulate and separate as amorphous bodies from a supersaturated solution, the rate of coagulation being affected by such small quantities of electrolytes as to preclude the possibility of the reaction being solely a chemical one. The evidence points further to the fact that with a certain and definite concentration of gypsum maximum hydration is attained, at the same time the rate of coagulation is reduced to a minimum, and the time of set is lengthened.

(*C*) *Calcium Sulphoaluminate Hydrated.*—An interesting feature of these microscopic examinationswas the isolation and identifica-

[29] J. Ind. Eng. Chem., 4, pp. 110–114; February, 1912. [30] Hydraulic Cements, p. 341; 1904.

tion of calcium sulphoaluminate crystals. An increase in the amount of plaster showed a steady increase in the amounts of sulphoaluminate crystals, and above 3 per cent plaster a constantly increasing amount of gypsum crystals was noted. The extension of these tests to 28 days resulted chiefly in an increase in the amount and size of the hydrated tricalcium aluminate plates, no amorphous material except hydrated alumina (in the case of the 5:3 calcium aluminate and the monocalcium aluminate) being present at the end of this period. It was also noted that the sulphoaluminate needles could be found only in the undried specimens, since drying at 100° resulted in the formation of hydrated tricalcium aluminate and peculiar club-shaped crystals of calcium sulphate differing in their optical properties from normal gypsum. The optical constants pointed to a compound having a composition somewhere between that of anhydrite and gypsum.

To study further the composition of sulphoaluminate, a sample of tricalcium aluminate was shaken with water and rapidly filtered into a clear saturated calcium sulphate solution. At the end of one-half hour there was a faint cloudiness in the solution which persisted for several days, and finally a few flakes or scales were deposited on the side of the containing vessel. As they were very few in number, a solution of lime hydrate was added, and immediately a white, apparently gelatinous, precipitate formed, which on microscopical examination proved to be homogeneous and consisted of minute prismatic crystals.

In order to increase their size the solution was allowed to evaporate spontaneously in a vacuum desiccator over concentrated sulphuric acid until the solution was reduced to about one-third of its original bulk. It was then rapidly filtered, washed with lime hydrate solution, alcohol, and ether, and air dried for two hours. The analysis of the crystals showed:

	Per cent composition	Molecules
CaO	26.1	6.0
Al_2O_3	7.8	1.0
SO_3	19.9	3.0
H_2O	46.1	36.5

Hence the formula of the calcium sulphoaluminate crystals is $3CaO.Al_2O_3.3CaSO_4.36\frac{1}{2}H_2O$.

Another sample was washed with limewater, alcohol, ether, and sucked dry with the filter pump. Its formula was found to be $3CaO.Al_2O_3.3CaSO_4.42H_2O$. These needles (see Fig. 12) were identical optically with those observed by hydrating the aluminates on a slide with a saturated gypsum solution.

There is considerable variation in the water content reported by various experimenters, such as 19.5 per cent by Klinkenberg,[31] 55.71 per cent by Candlot,[32] 30 per cent by Michaelis,[33] and 28.5 per cent by Deval.[34]

These variations in water content indicate the ease with which it loses water, all of it being lost at 100°. The unsuccessful attempts by Bates [35] to produce a compound of this composition were due to the fact that fused tricalcium aluminate was used. This compound contained besides tricalcium aluminate, 5:3 calcium aluminate, and free lime. The latter two compounds were formed through the partial disassociation of the tricalcium aluminate at its melting point. On treating it with water gelatinous aluminum hydroxide was formed and was filtered out with the rest of the precipitate, thus upsetting the balance of the elements in the analysis.

(*D*) *Hydration on Slides.*—The method followed was the same as that employed in the similar investigation with water. In this case, however, a saturated solution of calcium sulphate was used. Tricalcium aluminate began to hydrate almost immediately with the formation of needles and plates of hydrated tricalcium aluminate. Shortly, however, there began to form extremely fine needles (see Fig. 13), which were very difficult to observe and could be seen only when the cone of light from the substage of the microscope was reduced to almost vertical rays by closing the substage diaphragm. Even then they could be detected only after careful study. These needles, while always remaining long and slender, grew in size and thickness until interference colors were

[31] Dingler's Poly. J., **249**, pp. 89–95; 1894.
[32] Bull. Soc. D'Encouragement, **73**, pp. 685–716; 1890.
[33] Proc. Inst. Civil Eng., **107**, p. 370; 1892.
[34] Bull. Soc. D'Encouragement, pp. 30–54; January, 1900.
[35] Tech. Paper, Bureau of Standards, No. 12, pp. 37–39; 1912.

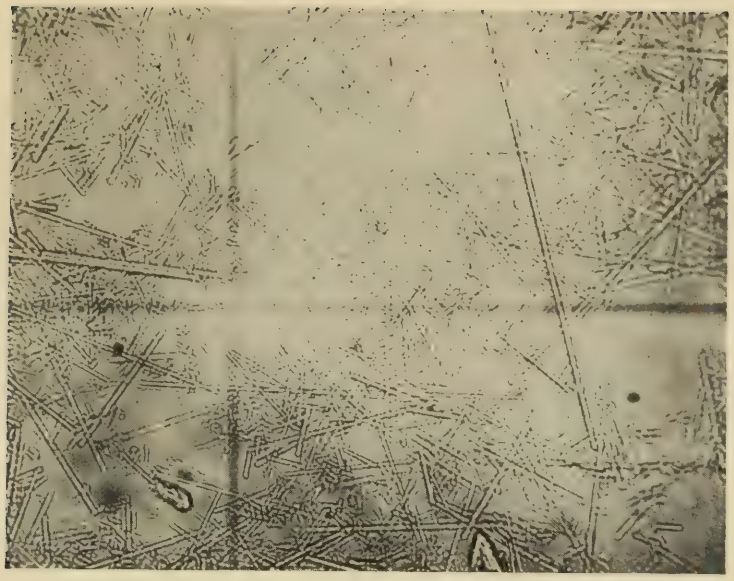

FIG. 12.—*Showing long slender needles of calcium sulphoaluminate obtained by the reaction of solutions of tricalcium aluminate and calcium sulphate. This was taken without nicols and the magnification = 400 diameters*

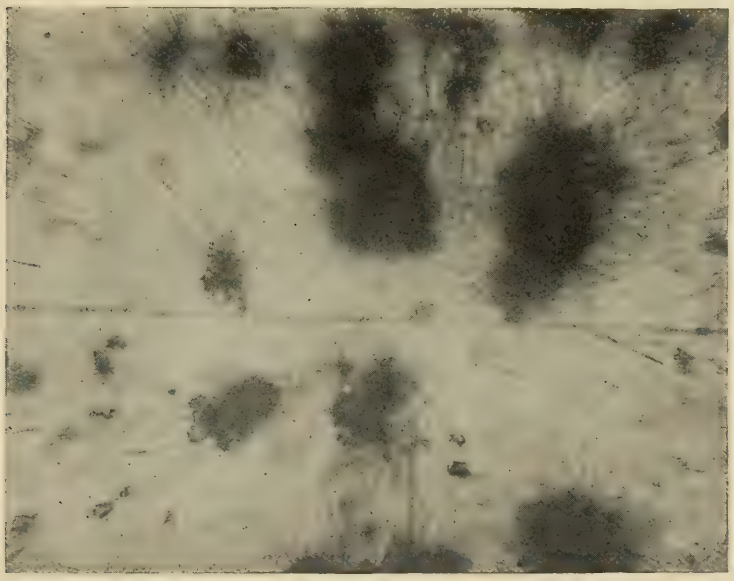

FIG. 13.—*Showing fine needles of calcium sulphoaluminate observed on a slide of tricalcium aluminate hydrated in a calcium sulphate solution. This was taken without nicols, and the magnification = 280 diameters*

observed with crossed nicols. The maximum color noted was white of the first order, showing a low double refraction.

In order to study more carefully the optical constants of this new compound, a slide was hydrated until apparent maximum crystal growth was attained. It was then dried in a vacuum desiccator, care being taken not to dry too long, since it was found that sulphuric acid absorbed the water of crystallization from the sulphoaluminate crystals. Generally about one hour was sufficient to dry the slide.

Microscopic observations of the sulphoaluminate crystals showed their long prismatic development. Twinning was not noted, but occasionally irregular intergrowths were observed. The crystals showed low interference colors ranging from black to white of the first order. The character of the principal zone was negative and the extinction parallel. The indices of refraction could not be obtained quantitatively, since they were lower than 1.48 (the lowest index in our series of immersing liquids). The interference figure was biaxial with a large optic axial angle. Owing to the low double refraction the interference figures showed only black bars with hazy outlines, and no color isogyres were noted. The optical character was positive. These crystals could easily be distinguished from the hydrated tricalcium aluminate crystals by their lower double refraction, different character of their principal zone, and different prismatic development, the terminations being flat, perpendicular to the long axis of the prism, and not pointed, as in the case of the hydrated tricalcium aluminate.

The 5:3 calcium aluminate slide started to hydrate very soon with the formation of amorphous material, spherulites, needles, and hexagonal plates noted in the hydration of slides with water. At the same time crystals of sulphoaluminate were formed having optical properties identical with those observed in the hydration of tricalcium aluminate in calcium sulphate solution. They were, however, larger and more easily observed. As in the previous case the specimen was dried in the desiccator and examined while immersed in liquids of known refractive indices.

The monocalcium aluminate slide hydrated in a short time and gave the same resulting products as the 5:3 calcium aluminate

slide. The amount of amorphous hydrated alumina was greater and the crystals of sulphoaluminate were better developed. The optical constants of the latter were identical with those of the sulphoaluminates observed on the tricalcium aluminate and 5:3 calcium aluminate slides, and as has been stated before, they were identical with the needle crystals obtained by the action of a solution of tricalcium aluminate on a saturated calcium sulphate solution.

Hydration on slides with mixtures of one part lime hydrate and one part calcium sulphate solution gave no new hydration products but increased the quantity of sulphoaluminate crystals.

(*E*) *Hydration in the Autoclave.*—No sulphoaluminate needles were observed in any specimens which were exposed to the autoclave test, and, as Kühl [36] has pointed out, the heat of the steam bath is sufficient to break up the compound into its component constituents. However, club-shaped crystals were noted. As had been noted before, from optical considerations these crystals have a composition between that of gypsum and that of anhydrite. They have a higher index than the former; $\alpha = 1.561 \pm 0.003$ and $\gamma = 1.577 \pm 0.003$. The crystals show parallel extinction, medium low double refraction, and interference colors of the first order. The character of the principal zone is positive, and the interference figures are biaxial.

That these club-shaped crystals are intermediate in composition between gypsum and anhydrite is shown by the fact that the index of refraction and the double refraction are both greater than that of gypsum and less than that of anhydrite. The extinction is identical with that of the latter.

Monocalcium aluminate hydrated with various amounts of plaster at 300 pounds pressure for two hours showed amorphous material, and a few hexagonal and needle crystals of hydrated tricalcium aluminate. The same was true of 5:3 calcium aluminate, which showed an increase in the content of hydrated tricalcium aluminate crystals. With tricalcium aluminate very large plates and needles of hydrated tricalcium aluminate were found.

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[36] Mitt. Zent. Ford. Deut. Port. Cement. Ind., 2, pp. 108–110; 1913.

With the aluminate containing free lime, very large crystals of calcium hydroxide were found in addition to the other products of hydration. The effect of adding hydrated lime to the plaster and aluminate was simply to increase the amount of amorphous material, no effect on crystallization being noted.

It was found that the water of hydration could likewise be partially driven out of the amorphous hydration product of the aluminates and the refractive index raised by holding the pressure at 400 pounds for four hours and maintaining the samples in an atmosphere of steam. In the other cases where the specimens were kept in water in the autoclave during the test there was still a slight rise in refractive index but not as great as before. The conditions attained were sufficient to drive out a part of the water. So the water content in any hydrated aluminate specimen is largely dependent on how it is dried.

III. SILICATES (INCLUDING MIXTURES OF SILICATES AND ALUMINATES)

1. HYDRATION OF CALCIUM METASILICATE ($CaO.SiO_2$)

Calcium metasilicate was prepared like the other specimens by burning in the updraft kiln. It was found to be pseudowollastonite. It occurred in irregular intergrown grains showing no crystalline outline, had a high double refraction, white of the highest order being the maximum color observed. The refractive indices were $\alpha = 1.61 \pm 0.003$; $\gamma = 1.65 \pm 0.003$. $\gamma - \alpha = 0.04$. The biaxial interference figure was very characteristic, but in many cases it was difficult to distinguish it from a uniaxial figure, since the optic axial angle was very small. The optical character was positive. No free lime was observed in this specimen. The chemical analysis showed:

	Per cent
SiO_2	51.45
Al_2O_3	.17
Fe_2O_3	.08
CaO	48.16
Ignition loss	.18

(See Tables 2 and 3.)

Neither in steam at atmospheric pressure nor by hydration in water did calcium metasilicate take up any water, nor was there

any hydration on a slide. By placing the material in a metal receptacle containing water and placing the whole in an autoclave for two hours at 300 pounds an extremely slight etching of the crystals was obtained, but the amount of water taken up was insignificant. All attempts to hydrate it in saturated limewater and in saturated calcium sulphate solution on slides gave negative results. The examination of slides containing mixtures of the silicate with each of the three aluminates in water, limewater, and calcium sulphate solutions showed that the silicate did not hydrate, but that the aluminate gave the same hydration products as when they alone were hydrated in these solutions.

2. HYDRATION OF GAMMA-CALCIUM ORTHOSILICATE ($\gamma 2CaO.SiO_2$)

Gamma-calcium orthosilicate was very readily prepared by mixing the materials in proper proportion and burning in a pot furnace. The specimen was then removed from the furnace while red hot and allowed to dust down in the open air. Much dusted material passed readily through the 200-mesh sieve without any further grinding. The gamma-orthosilicate as prepared consisted of very small prismatic crystals with a fair cleavage parallel to the prism axis. The cleavage, however, was not very generally observed. No twinning was noticed. The refractive indices were: $\alpha = 1.641 \pm 0.002$, $\beta = 1,645 \pm 0.003$, $\gamma = 1.655 \pm 0.002$. The interference colors were generally white to yellow of the first order. Double refraction (measured) = 0.015 ± 0.003. The extinction was parallel in most cases; sometimes, however, inclined extinction was observed, the maximum angle being about 3°. Biaxial interference figures were observed with the angle of the optic axis perpendicular to the prism axis. The optical character was positive. The chemical analysis showed:

	Per cent.
SiO_2	34.58
Al_2O_3	.60
Fe_2O_3	.16
CaO	64.63
Ignition loss	.07

By heating the silicate in steam at atmospheric pressure at 110° for four hours, 0.52 per cent of water was taken up. Micro-

scopically the material was but slightly altered. A little etching on the edge of some of the grains was observed, and a few small doubly refracting grains of lower index were noted, but they were too minute for further identification. Attempts to hydrate the material in water or in the autoclave gave similar results, extremely small amounts of water being fixed. Hydrated on a slide with water, limewater, or gypsum, it likewise showed no change. No hydration of this silicate was noted on mixing it with any of the aluminates, with plaster, or with limewater and storing in water.

3. HYDRATION OF BETA-CALCIUM ORTHOSILICATE ($\beta 2CaO.SiO_2$)

(*A*) *Preparation.*—True to the reports of previous investigators, great difficulty was encountered in preparing this compound. It was not possible to secure temperatures in the kiln much over 1,500°, and this temperature was not sufficient to prevent dusting of the material when taken from the kiln, even after plunging it under water or under mercury. By burning in a pot furnace, a higher temperature was reached, but considerable quantities of magnesia were found in the beta-calcium orthosilicate thus prepared. In some cases the specimens were colored brown due to iron. These contaminations resulted from the volatilization of magnesia and ferric oxide in the magnesite brick. Finally, recourse was had to an electrical resistance furnace of the type used by the Ceramic Division of the Bureau for determination of melting points (see Fig. 14).

The magnesite plug at the bottom supported the specimen within the hot zone. By this means the specimens could be rapidly withdrawn from the furnace and plunged into water or mercury. This, however, was found to be unnecessary, since no tendency toward dusting was noted on removal of the material from the hot furnace. It should be noted also that small amounts of magnesia were added to prevent dusting. Considerable difficulty was found with the refractory lining used, as it cracked under conditions of rapid heating and rapid cooling to which it was subjected. Fused magnesia with magnesium chloride, alundum, ground magnesite brick, magnesia with alumina, and magnesia

with feldspar were tried. The most satisfactory mixture consisted of thirty parts of feldspar and seventy parts of magnesia, intimately mixed, ground, molded with water, and given a preliminary firing in the pot furnace. This lining showed no tendency

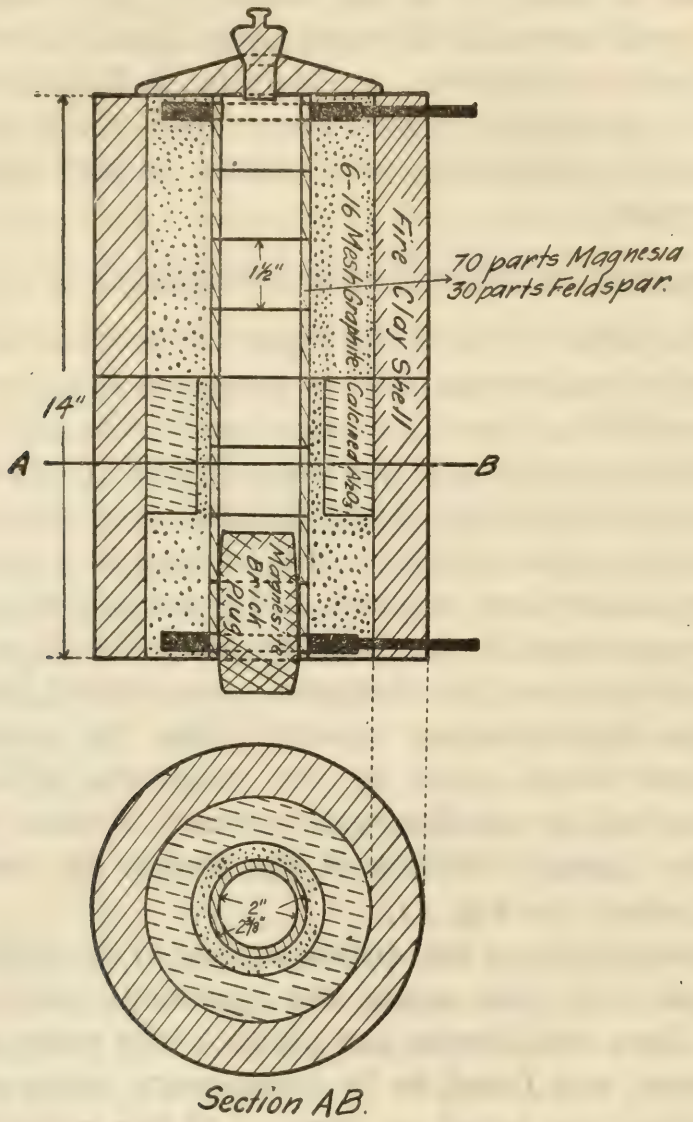

FIG. 14.—*Showing carbon resistance furnace*

toward cracking, but under the severest conditions they grew a little soft, during a prolonged run.

The beta-calcium orthosilicate prepared consisted chiefly of overlapping grains, some without definite outline and some showing prismatic development. No twinning was observed. Cleavage was noted parallel to the prism axis, and extinction was parallel.

The refractive indices were $\alpha = 1.720 \pm 0.003$, $\gamma = 1.735 \pm 0.003$. Maximum interference color observed was yellow of the second order. Biaxial interference figure was noted with a large optic axial angle. The chemical analysis showed:

	Per cent.
SiO_2	35.21
Al_2O_3	.56
Fe_2O_3	.21
CaO	63.53
MgO	.37
Ignition loss	.22

The fact that magnesia prevents dusting of the orthosilicate was noted by Le Chatelier,[37] Sefetrom,[38] and by this laboratory [39] in their work on magnesia in Portland cement. A very small amount was sufficient to accomplish this, although the burning temperature was found to be a great factor. No beneficial action was noted from the presence of magnesia when the specimens were burned in the pot furnace at 1500° C.

(*B*) *Hydration in Steam at Atmospheric Pressure and in Autoclave.*—Unexpected difficulties were met in attempting to hydrate beta-orthosilicate as it appeared extremely reluctant to take up water. Heating it in steam at temperatures from 105 to 140° caused no water absorption and no visible change in the material. Likewise there was no hydration when it was allowed to stand with an excess of water except after a considerable length of time when there was an extremely slight hydration. On exposing the material to both steam and hot water in the autoclave, only a slight etching of the crystal edges and formation of a little isotropic hydrated material was noted.

(*C*) *Hydration on Slide with Water.*—Beta-orthosilicate mixed with a large excess of water on a slide underwent no change until after six weeks, when a very slight etching of some of the grains was noted, and a slight amount of isotropic hydrated material was observed.

(*D*) *Hydration with Calcium Hydroxide.*—Only a slight action on the beta-orthosilicate was noted when it was hydrated with lime hydrate solution for seven days. Grinding with high-

[37] Ann. Mines, **170**, pp. 388–412; 1887.
[38] J. für Tech. u. Okonom. Chemie., **10**, p. 145; 1831.
[39] Orig. Com., 8th Int. Cong. Applied Chem., **5**, pp. 73–81; 1912.

burned lime and then adding water did not increase the hydration. The silicate crystals in both cases were etched especially along the edges, where the refraction was lowered and a slight amount of amorphous material formed. The same results were obtained in the autoclave, only to a greater extent.

Continuing the tests to 28 days, samples of beta-orthosilicate were gauged with limewater and molded into small cylinders. After 24 hours these were removed from the molds and immersed in water for 27 days. At the end of this time the specimens were soft, friable, and consisted almost entirely of unchanged silicate surrounded by a thin layer of amorphous hydrated material. Continuing the tests to 90 days the hydration became more marked. Nevertheless, there remained considerable unhydrated silicate even at this period.

The inability to hydrate beta-orthosilicate prevented the determination of the temperatures above which it loses water. Bied states that this temperature for the basic silicates is 140°, while Ljamin [40] states that the bound water of the silicate is lost at 150°.

Burian and Seber,[41] who studied the hydrolysis of cements by conductivity measurements, found that hydration took place much more rapidly in limewater than in distilled water. However, at best there were observed only a small increase with limewater. Probably the small amounts of other materials in cement, such as alkali and ferric oxide, play some part.

Very conflicting results are reported as to the hardening of beta-orthosilicate with water. Le Chatelier [42] found that neither water nor limewater had any effect on it. Bied [43] has noted the inertness of beta-orthosilicate toward hydration. He baked tablets of this composition containing 2–3 per cent R_2O_3 to 1600–1700°, ground the specimens, mixed them with water, and stored them under water for one year. At the end of this time they had no appreciable strength. Richardson [44] thought it had little hydraulicity except in the presence of carbon dioxide and while

[40] Protocol, German Port. Cement Mnfrs. Assoc., p. 52; 1898.
[41] Chem. Listy, **6**, pp. 145–149; 1912.
[42] Ann. Mines, **170**, pp. 388–412; 1887.
[43] Proc. Int. Assoc. Mat. **2**, (9), p. 8; 1911.
[44] Cement, **5**, p. 117; 1905.

setting slowly in water was not volume constant. Newberry [45] states that the silicate set hard in 7 days and boiled sound, and whether fused or not it maintained its previous composition and lost very little lime. Schott [46] made a product that set in 24 hours and hardened well in 8 days. Unger [47] found that his stable material after mixing with water gave a strength of 140 pounds in 8 weeks, part of this being due to carbonation from carbon dioxide in the air. It is interesting to note that as early as 1865 Heldt [48] was able to obtain hardening mixtures from lime and alkali silicates, Oddo [49] likewise agreed with Le Chatelier in being unable to prepare a product which would harden with water.

(*E*) *Hydration with Calcium Sulphate Solution.*—Mixing the silicate with a saturated solution obtained from plaster gave no appreciable hydration, and treatment in the autoclave resulted only in the previously noted change in the gypsum.

(*F*) *Hydration with a Large Excess of Solution.*—As it is generally considered that a large excess of water hastens the hydration of cement, the effects of an excess of solution on the beta-orthosilicate were studied. Efforts were made to hasten its hydration by placing 1-gram samples in tall glass-stoppered cylinders, to which were added 150 cc of one of the following liquids: Water, saturated tricalcium aluminate solution, saturated limewater, saturated calcium sulphate solution, a solution made by shaking freshly precipitated and well-washed aluminum hydrate with a large excess of water and filtering, and a 2 per cent solution of aluminum sulphate. The cylinders were well shaken and rotated in a slow-moving stirring apparatus for 10 days. At the end of the second day there was noted with the tricalcium aluminate solution a slight permanent suspension in the cylinder, while the others settled out to a precipitate and a perfectly clear solution in less than a minute. At the end of the tenth day a very large amount of permanently suspended material was noted in the tricalcium aluminate solution, while the limewater and the calcium sulphate, etc., solutions contained only a little flocculent material in addition to the precipitate.

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[45] Bull. Soc. D'Encouragement, **99**, p. 647; 1903.
[46] Cement Eng. News, **22**, p. 287; 1910.
[47] Cement Eng. News, **22**, p. 287; 1910.
[48] J. Prakt. Chem., **94**, p. 129; 1865.
[49] Accad. dei Lincei, **26**, p. 361; 1896.

After drying, the product was examined microscopically. The material treated with the aluminate solution still contained some unhydrated beta-orthosilicate and a considerable amount of the isotropic amorphous material. The silicate hydrated in the other solutions showed considerably less hydration in the following decreasing order: Calcium sulphate, limewater, aluminum sulphate, hydrated alumina, and water. The products of hydration were identical in each case and consisted of amorphous material. No calcium hydroxide was present.

After washing and drying all the treated specimens for two hours at 100° the ignition losses were as follows:

	Per cent.
Tricalcium aluminate solution	4.04
Plaster solution	1.94
Lime hydrate solution	1.73
Aluminum sulphate solution	1.38
Aluminum hydrate solution	1.04
Water	0.97

(*G*) *Inversion of Beta-Orthosilicate to Gamma-Orthosilicate.*—It must be noted that beta-orthosilicate, after being given a steam treatment and dried on the hot plate for the determination of the water, showed considerable amounts of the gamma form. This effect was also noted in the material ground to about six-mesh size and stored in bottles. There was a slow accumulation of powder at the bottom of the bottles which proved to be gamma-orthosilicate. The rate of its formation, however, was not constant, the largest amounts being formed within two or three days after the burning of the specimen. Further dusting proceeded slowly. It is evident that heat accelerates this change, and, furthermore, it is found that dusting proceeds more quickly in specimens where the beta-orthosilicate is very fine grained. In specimens containing larger crystals, due evidently to prolonged heat treatment, there was not the slightest evidence of dusting even at the end of three months.

4. HYDRATION OF BETA-CALCIUM ORTHOSILICATE AND ALUMINATES

(*A*) *Hydration in Steam at Atmospheric Pressure.*—To observe any possible action of the aluminates on beta-orthosilicate at atmospheric pressures, mixtures of 70 parts of silicate and 30

parts of aluminates were first ground together and then treated with steam at temperatures up to 140°. Microscopical examination showed that the aluminate alone had been hydrated. These tests were made with each of the three aluminates. To insure better contact of the material the mixtures of silicate and aluminate were placed in small linen bags which were then sewed up and treated with steam with like results.

It was realized that even with the very finest grinding of the mixture the intimate contact of aluminate with silicate in a cement could not be reproduced. Therefore, a number of cements were heated in steam for as long as four hours at temperatures ranging from 105° to 140°. In every case the amount of water absorbed was from 3 to 6 per cent, and in no case was the beta-orthosilicate hydrated.

(*B*) *Hydration in the Autoclave.*—Corresponding tests in the autoclave showed a slight etching of the silicate crystallites with the usual hydration of the aluminates. A mixture hydrated in an excess of water for 24 hours then placed in the autoclave showed no more hydration than that noted in the autoclave alone.

(*C*) *Hydration of Molded Specimens.*—Mixtures of beta-orthosilicate with monocalcium aluminate, 5:3 calcium aluminate, and tricalcium aluminate, respectively, and a small amount of plaster were hydrated in limewater and in water for 28 days. A slight increase in the amount of hydrated material was noted with limewater over that with water. The specimens were somewhat friable but stronger than the 28-day hydration specimen of the beta-orthosilicate hydrated in a solution of tricalcium aluminate. One peculiarity was noted in that on the outside of the specimens glistening crystals were seen, which in some cases could be picked off with the forceps. Microscopical investigation proved these to be hydrated tricalcium aluminate. In addition there were a few calcium carbonate crystals resulting from the decomposition of the aluminates by the carbon dioxide in water. Very few small crystals were noted when the specimens were broken open. The indications are that there was a diffusion of aluminate from the interior to the surface followed by crystallization.

(*D*) *Hydration on Slides.*—In this series mixtures were made of about three parts of beta-orthosilicate to one part of each of the

following: Tricalcium aluminate, 5:3 calcium aluminate, and monocalcium aluminate. This ratio was used to conform to the approximate quantitative relationship of the above compounds in a Portland cement. The same procedure was followed as with all previous hydrations on slides.

With beta-orthosilicate and tricalcium aluminate the first effect noted was the immediate beginning of hydration of the aluminate. This, when hydrated, formed needles and plates of hydrated tricalcium aluminate, similar to those previously observed. At the end of two days the silicate showed signs of being etched, and a little amorphous material was noted along the edges of the silicate grains. The etching continued and at the end of a week the amorphous material was fast surrounding the silicate crystallites. At three weeks practically the whole slide was covered with amorphous material; but the aluminate needles and plates were unchanged, although their definiteness of outline was often obscured by the amorphous silicate material. (See Fig. 15.) No calcium hydroxide crystals were observed. A slide dried in an atmosphere free from carbon dioxide and treated with White's solution showed the absence of amorphous calcium hydroxide.

None of the crystallized needles of hydrated silicate noted by previous investigators, Kaisermann,[50] for instance, were observed. Recourse was had to a paraboloid condenser for dark field illumination, which Kaisermann states was necessary for the observation of these needles. Again nothing was observed but amorphous material, having no definite crystalline outline whatsoever. Furthermore, according to Kaisermann, an excess of water prevented the formation of these needle crystals, and insufficient water caused the preparation to dry before there was opportunity for crystallization. Under the assumption that too much or perhaps too little water was used in the preparation, a series of five slides were made up with varying amounts of water. In every case the hydration products were the same as previously noted. In no case were there any fine needle crystals of silicate observed. Needles of hydrated tricalcium aluminate were of course noted; but they could not be confused with the silicate

[50] Cement and Eng. News, 23, p. 62; 1911.

needles, for, according to Kaisermann, the latter have a different crystal development and show almost no double refraction.

Michaelis [51] in commenting on the needles of lime silicate observed by Kaisermann, states that the latter did not prove their composition and that they may be zeolite, gypsum, or sulpho-aluminate crystals. The fact that Kaisermann observed these crystals in mixtures supposedly made from lime and silica would probably preclude the possibility of their being either gypsum or sulphoaluminate crystals. On the other hand, he states they were more readily observed in puzzolana cements. Puzzolana cements, puzzolana, trass, tufa, etc., contain soluble silica which combines with lime. In addition, they contain zeolites which exchange their base for lime on coming in contact with the latter. So it seems possible that the crystals observed were formed by the presence of impurities in the silica used.

A slide of beta-orthosilicate and tricalcium aluminate was dried in an atmosphere free from carbon dioxide after the hydration was apparently completed. It was then hydrated again on a slide with more water. The hydrated silicate again showed no needle development, but occurred in amorphous round grains. No splitting off of calcium hydroxide was observed.

The first effect of the hydration of beta-orthosilicate and 5:3 calcium aluminate was the formation of radial spherulites and the subsequent growth of needles and plates of hydrated tricalcium aluminate, together with the formation of some amorphous material. The silicate started to hydrate within two days with the formation of amorphous gelatinous material, which at the end of 16 days covered the whole slide. No calcium hydroxide was observed in any form and no needle crystals of hydrated silicate were noted. Similar slides were also prepared with varying amounts of water, and observations were made with dark field illumination, but no silicate needles were found. No hydration product of the silicate was observed which possessed even the slightest double refraction.

The slides of monocalcium aluminate and beta-orthosilicate behaved much like those of the preceding series. The aluminate

[51] Cement and Eng. News, 23, p. 57; 1911.

hydrated first with the splitting off of considerable hydrated alumina and the formation of needles, plates, and spherulites of hydrated tricalcium aluminate. The silicate commenced to hydrate in a couple of days to the previously observed amorphous material, which at the end of a week covered the whole slide and was so thick as to preclude further observation.

No reason for the behavior of the aluminates in hastening the hydration of the beta-orthosilicate has been found, other than that it is simply a case of the silicate being more soluble in the aluminate solution than in water, and that a saturated solution is formed with subsequent precipitation of the amorphous hydrated silicate.

5. HYDRATION OF TRICALCIUM SILICATE ($3CaO.SiO_2$)

(*A*) *Preparation.*—Tricalcium silicate was prepared by mixing calcium carbonate, to which a small amount of magnesia had been added, and silica in the proper proportion with water, and molding the mixture into hollow cylinders. These were dried and burned in a pot furnace at 1500° C. The specimens were then withdrawn from the furnace and allowed to dust down. The coarser particles of the resultant product were ground until all the material passed the 200-mesh sieve. The powder was then remolded with a dilute sugar solution, as it formed a very granular mass with water alone, which on drying out fell to pieces. These cylinders were burned in the electric furnace. No temperature measurements were made, but the specimens were examined with the microscope after each burn to observe the progress of the formation of tricalcium silicate. After one burn in the electric furnace, a nondusting mixture of beta-calcium orthosilicate and comparatively large round grains of free lime was found. After regrinding the powder was moistened with alcohol, remolded, and reburned for about five hours. This process was repeated three times before the material was found to be satisfactory. Entire homogeneity was never obtained, since the best product contained a few scattered grains of free lime, beta-calcium orthosilicate, and tricalcium aluminate. However, the hydration of these small amounts of impurities could in no way be confused with the hydration of the major portion of the product.

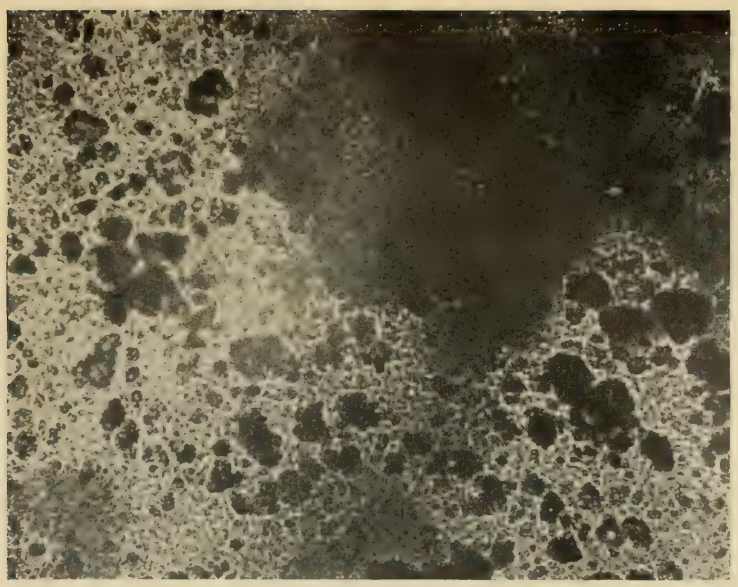

FIG. 15.—*Showing amorphous, hydrated silicate on a slide of beta-calcium orthosilicate and tricalcium aluminate in water. The amorphous material covered the whole slide and obliterated the hydrated tricalcium aluminate crystals present. This was taken without nicols, and the magnification = 200 diameters*

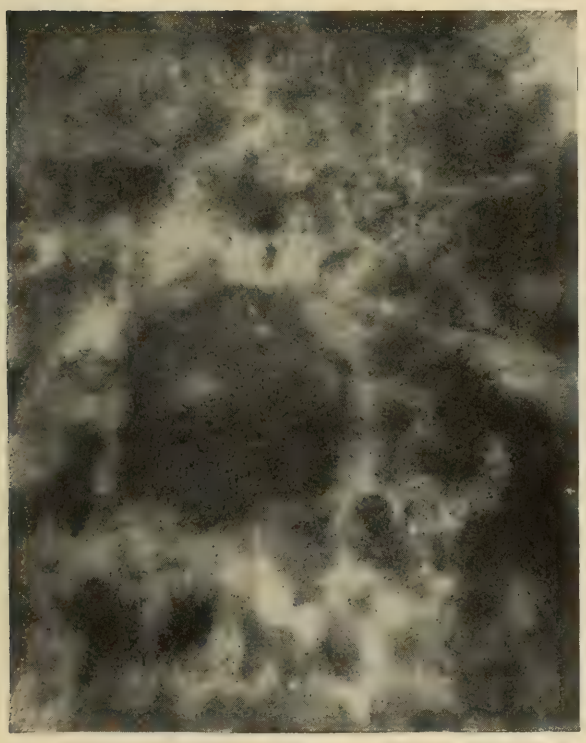

FIG. 16.—*Showing tricalcium silicate and tricalcium aluminate in water, taken without nicols. Note the large hexagonal calcium hydroxide crystal and the smaller needles of hydrated tricalcium aluminate covered with and obscured by amorphous hydrated silicate. Magnification = 160 diameters*

FIG. 17.—*Showing tricalcium silicate and 5:3 calcium aluminate, taken with crossed nicols. Note the large calcium hydroxide crystals, the spherulites and needles of hydrated tricalcium aluminate. The amorphous material can not be observed with crossed nicols. Magnification = 165 diameters*

The trisilicate consisted of minute crystallites, showing no definite crystal outline. The mean index of refraction was 1.715 ± 0.003. The double refraction was extremely low, the maximum interference color observed being a first order grayish white, while many of the grains were practically isotropic. Interference figures were observed with difficulty on a few favorable grains, and the compound was found to be biaxial with a very small optic axial angle. The optical character is negative. No twinning lamellæ whatever were noted. The chemical analysis showed:

	Per cent.
SiO_2	26.12
Al_2O_3	.21
Fe_2O_3	.09
CaO	72.62
MgO	.93
Ignition loss	.09

(*B*) *Hydration of Molded Specimens in Water.*—A noticeable feature of the hydration of the tricalcium silicate was the rapidity with which it took place. A specimen mixed with 20 per cent of water set hard at the end of five hours without any noticeable evolution of heat, and specimens kept 28 days in water showed no signs of cracking or disintegrating. This is in noticeable contrast to the mixtures of beta-orthosilicate with as much as 50 per cent high-burned free lime. In this case the material was soft and friable after 24 hours and fell away to a soft mush in the water; and very small amounts of amorphous hydrated silicate were found, while with the trisilicate large quantities were observed.

(*C*) *Hydration in Steam at Atmospheric Pressure and in the Autoclave with Water.*—On treating tricalcium silicate in steam at temperatures both below 140 and up to 200° C from 0.5 to 0.7 per cent of water was taken up. The fact that water was absorbed at high temperatures must be due to the hydration of the free lime present, as a small amount of calcium hydroxide was always found present after these tests.

In the autoclave, it was possible to hydrate completely the trisilicate after it was allowed to harden for 24 hours with water, so that no grains with unhydrated centers remained. The hydration products were crystals of calcium hydroxide and amorphous hydrated silicate. On the other hand, mixing the beta-orthosilicate

with one-third of high-burned lime showed the silicate to be almost completely unhydrated after the autoclave treatment. A further effect noted was that raising the pressure in the autoclave from 150 to 600 pounds per square inch resulted in an increased size of the calcium hydroxide crystals.

(*D*) *Hydration on Slide with Water.*—Hydrating the tricalcium silicate with water on a slide resulted in the formation of a few crystals of calcium hydroxide and amorphous hydrated silicate within 24 hours. The hydration continued with the formation of more and larger calcium hydroxide crystals and considerable amorphous material, until at the end of three weeks the latter covered the slide completely. The calcium hydroxide crystals were orientated generally in one of two ways, either perpendicular to the "c" crystallographic axis or parallel to it. When perpendicular to "c" they were hexagonal in shape, showed little or no double refraction, and gave typical uniaxial interference figures perpendicular to "c" with negative optical character. When parallel to the "c" axis they showed prismatic development, medium high interference colors often of the third order, depending upon the thickness of the crystals, parallel extinction and the interference figures consisted of two rapidly separating hyperbolæ characteristic of uniaxial crystals orientated parallel to "c." The amorphous material was gelatinous in appearance. No needles were observed.

(*E*) *Hydration with Plaster.*—Using the tricalcium silicate with plaster and varying the amount of the latter, no differences were noted except in the amount of gypsum crystals which increased with the percentage of plaster. This was the case with both slides and molded specimens. Hydration in the autoclave increased the size of the calcium-hydroxide crystals greatly.

(*F*) *Hydration with Limewater.*—Tricalcium silicate, hydrated on a slide with limewater, showed the same products as that hydrated in water. The rate of hydration was not apparently changed, since the amorphous material and calcium-hydroxide crystals began to be formed within 24 hours.

(*G*) *Influence of Tricalcium Silicate on Hydration of Beta-Calcium Orthosilicate.*—Mixing tricalcium silicate in varying amounts with beta-orthosilicate and plaster and hydrating in the autoclave had

no favorable influence on the hydration of the orthosilicate while the trisilicate was completely hydrated.

6. HYDRATION OF TRICALCIUM SILICATE AND ALUMINATES.

(*A*) *Hydration on Slides with Water.*—Slides containing mixtures of tricalcium silicate and tricalcium aluminate and of tricalcium silicate and 5:3 calcium aluminate were hydrated in the same manner as the individual constituents. The aluminates began to hydrate almost immediately to form the aforementioned hydration products. Within 24 hours the silicate began to take up water, splitting off calcium-hydroxide crystals and forming the amorphous hydrated silicate. (See Figs. 16 and 17.)

In order to dispel any doubt as to the identification of the hexagonal hydrated tricalcium aluminate and the hexagonal calcium hydroxide plate crystals, slides containing each of the above compounds were dried in an atmosphere free from carbon dioxide and then immersed in a liquid of refractive index equal to 1.555. The large hydroxide plates had invariably a higher and the small aluminate plates a lower index than the liquid. (See description of their optical properties, pp. 8, 23.)

(*B*) *Hydration of Molded Specimens in Water, Limewater, and Calcium Sulphate Solution.*—Monocalcium aluminate, 5:3 calcium aluminate, and tricalcium aluminate were mixed with the tricalcium silicate in the proportion of 1:3, gauged with 20 per cent water, pressed in the molds, left for 24 hours, and then immersed in distilled water for 28 days. They were then dried and examined microscopically. In each case calcium-hydroxde crystals were observed, and complete hydration of the tricalcium silicate had taken place. The specimens were extremely hard, dense, and strong, and compared very favorably to the strongest 28-day neat cement briquets. No differences were noted in cases where either limewater or calcium-sulphate solution were used for gauging. Only in the case of tricalcium aluminate and tricalcium silicate gauged in gypsum was there any considerable quantity of sulphoaluminate needles noted, but they were not well developed. In another case a saturated solution of tricalcium aluminate was used for gauging, the specimen being immersed in water. At the

end of 28 days it was very hard and compact, and the surface was coated with calcium hydroxide crystals large enough to be picked off.

With regard to their time of formation, calcium-hydroxide crystals could be observed in a specimen four hours after mixing with water, and they constantly grew in size. However, at the end of 28 days they were not as large as those produced in the autoclave at 300 pounds pressure after 24 hours' hardening.

In only one combination was disintegration observed, this taking place in a 3:1 mix of tricalcium silicate with tricalcium aluminate gauged with a saturated calcium-sulphate solution and immersed in saturated limewater. After 10 days the specimen was badly cracked, and after 15 days it had disintegrated to a soft mass containing large calcium hydroxide crystals, well developed hydrated tricalcium aluminate, and sulphoaluminate crystals with much isotropic amorphous material. Suspended in the solution was an abundance of very fine crystals of sulphoaluminate, so fine as to appear megascopically like a gelatinous precipitate.

(*C*) *Hydration on Slides with Limewater and Calcium Sulphate Solution.*—The hydration on slides of mixtures of tricalcium silicate with the aluminates in limewater and plaster solution gave no new hydration products except crystals of calcium sulphoaluminate. The rates of hydration did not differ from the rates of hydration of the same mixtures hydrated with water.

So far as could be noted, the calcium-hydroxide crystals have no effect on the precipitation of sulphoaluminate crystals. The former are more or less inert and are not readily acted upon by White's solution, while the amorphous calcium hydroxide reacts, forming the characteristic hydrated calcium phenolate crystals in a few minutes. (See Fig. 18.) However, calcium hydroxide crystals are slowly acted upon by magnesium salt solutions, and the amount of magnesium hydroxide precipitated is very small in comparison with that produced by the amorphous hydroxide.

Owing to the limited amount of material available, no tests were made to determine the amount of lime split off from the tricalcium silicate. Le Chatelier[52] and others state the principal constituent of

[52] Bull. Soc. Chim., 42, pp. 82–89; 1900.

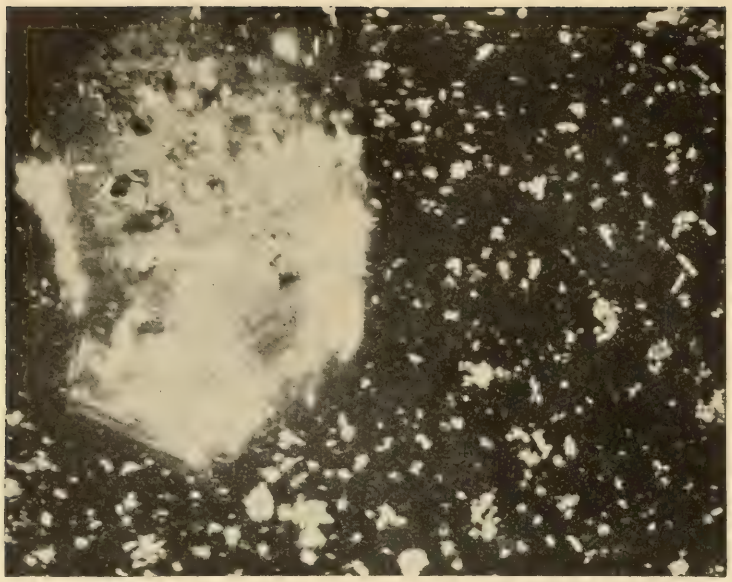

FIG. 18.—*Showing White's test on crystallized and amorphous calcium hydroxide, taken with crossed nicols. The large hexagonal plate is crystallized calcium hydroxide and is not affected. The amorphous hydroxide has been entirely converted into the characteristic prismatic crystals of calcium phenolate. Magnification = 280 diameters*

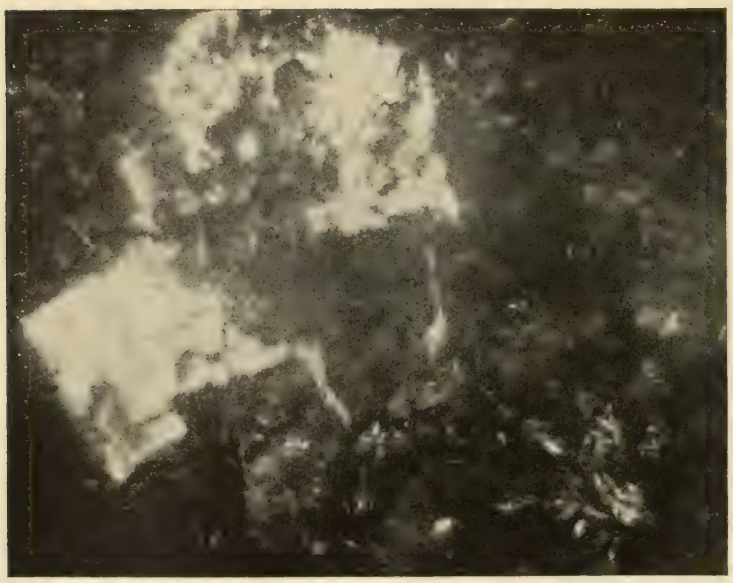

FIG. 19.—*Showing a white cement hydrated in water, taken with crossed nicols. Note the large calcium hydroxide crystals and the smaller hydrated tricalcium aluminate needles. These are more or less obscured by amorphous material. Magnification = 280 diameters*

hardened cements is a hydrated monosilicate ($CaO.\ SiO_2.\ 2\frac{1}{2}\ H_2O$). On the other hand there is the work of Newberry and Smith,[53] who found that one sample of supposed trisilicate, after shaking with water, gave a varying residue of 1.5 to 2 equivalents of CaO. to 1 of Sio_2 and a fused sample gave a hydrated silicate of the composition of $2CaO.\ SiO_2.\ 7H_2O$. In addition there is the interesting but little known work of Ferrari,[54] who found that the reaction proceeded as follows: $3CaO.\ SiO_2 + Aq = 2CaO.\ SiO_2.\ nH_2O + Ca(OH)_2$ and that the hydrated silicate formed yielded no more lime to water but lost lime on treatment with ammonium chloride solutions.

Again, Rebuffat [55] states that the calcium orthosilicate on hydrating does not decompose into calcium monosilicate and lime hydrate, since testing with sugar solutions showed that the composition of the material was very far from being calcium monosilicate.

IV. PORTLAND CEMENT

The hydration of cements were studied by slide tests, by the examination of molded specimens, and by means of the autoclave. For convenience in comparing the results they were tabulated, No. 1 being a white cement, No. 2 being another brand of white cement which contained 0.5 per cent CO_2 and 4 per cent H_2O, No. 3 a high silica slow-hardening cement, and No. 4 a dark-colored cement containing 8.97 per cent Fe_2O_3 and 3.64 per cent Al_2O_3. The chemical analyses are as follows:

	No. 1	No. 2	No. 3	No. 4
	Per cent	Per cent	Per cent	Per cent
SiO_2	25.02	23.68	24.59	20.37
Al_2O_3	6.08	5.10	6.49	3.64
Fe_2O_3	0.49	0.37	2.64	8.97
CaO	62.89	62.69	61.04	61.41
MgO	1.11	1.96	1.71	0.82
SO_3	1.75	1.37	1.45	1.19
Na_2O	0.11	0.03	0.12	1.54
K_2O	0.56	0.30	0.40	0.24
CO_2	1.08	0.51	0.93	1.04
H_2O	0.95	4.08	0.75	1.06

[53] J. Soc. Chem. Ind., **22**, p. 94; 1903.
[54] Ciment, **17**, pp. 81–85; 1912.
[55] Tonind. Ztg. **26**, p. 1579; 1902.

(*A*) *Hydration of Molded Specimens and Hydration in the Autoclave.*—The tabulated tests in Table 4 were made on fragments of briquettes made from neat cement and 18–20 per cent of water, stored in a damp closet for 24 hours, and then immersed in water. One of the interesting facts noted is the slow hydration of the beta-orthosilicate, the amount of which varies with different cements. Although a large number of samples have been examined, no definite rule has been evolved as to the rate of hydration of the beta-orthosilicate. Some cements contain a little hydrated beta-orthosilicate at the end of 7 days, while others contain very little at the end of 28 days. Some contain considerable unhydrated beta-orthosilicate at the end of 90 days. Perhaps the greatest factor resulting in the slowness of the beta-orthosilicate hydration in a cement is the size of grain. Microscopical evidence points to the fact that beta-orthosilicate in the larger cement grains is extremely slow to hydrate, while in the smaller grains it hydrates fairly readily. This is no doubt due to the comparatively small amount of surface that the large grains offer to the action of the aluminate solution. Again, the coating of amorphous hydrated calcium silicate appears to prevent the ready penetration of the water into the unhydrated interior of the grains.

The absorption of water by the different cements as tabulated below are of interest chiefly in connection with the autoclave hydration:

	No. 1	No. 2	No. 3	No. 4
	Per cent	Per cent	Per cent	Per cent
Hydration in water for 24 hours	8.24	7.72	5.48	5.42
Hydration in water for 7 days	10.88	8.84	8.92	9.74
Hydration in water for 28 days	13.76	13.78	13.48	14.06
Hydration in autoclave	11.00	10.86	9.86	10.86

The amount of water absorbed by the autoclave briquettes is significant on account of the considerable amount absorbed, and by the fact that the refractive index of the aluminate was raised and the optical properties of the gypsum changed. This indicates conclusively that a part of the water has been expelled.

(*B*) *Hydration of Cement on Slides.*—Slides were made up of a commercial white cement in an excess of water. (See Fig. 19.) The first effect noted was the beginning of the formation of hydrated tricalcium aluminate and calcium sulphoaluminate crystals which took place in a short time. The latter crystals were extremely fine and could readily be overlooked. At 24 hours these crystals had increased in size and numbers and the presence of a few lime hydrate crystals, together with a little amorphous material, showed that the tricalcium silicate was beginning to hydrate, while the beta-orthosilicate was quite unchanged. With time the number of calcium hydroxide crystals and the amount of amorphous material increased. Finally the latter covered the whole slide.

A slide consisting of a normal Portland cement in water started to hydrate quickly with the formation of hydrated tricalcium aluminate and calcium sulphoaluminate crystals. The hydration of tricalcium silicate was slow in starting, since calcium hydroxide crystals and the accompanying amorphous hydrated silicate were noted only after two days. The further hydration of this compound proceeded readily with the formation of more calcium hydroxide and amorphous silicate. After a week the beta-orthosilicate in the fine cement grains began to hydrate to the amorphous silicate, and this latter covered practically the whole slide.

A sample of normal cement hydrated with an excess of water in a well-stopped bottle for over a year showed hydrated tricalcium aluminate needles and plates, sulphoaluminate needles, calcium hydroxide crystals, calcium carbonate crystals, and amorphous material. Thus, even in a considerable length of time, an excess of water did not bring about the crystallization of the amorphous hydrated silicate.

(*C*) *Use of Large Volumes of Mixing Water.*—The tricalcium silicate is in most cases only slightly hydrated at the end of 24 hours, while the beta-orthosilicate has not reacted at all. Therefore, the use of large volumes of mixing water, as is done in mixing concrete to be spouted or sent through chutes, can be considered only in relation to the aluminates. In these tests, it has

been found that variations in the amount of water affected only the rate at which the aluminates hydrated and crystalized, the larger the amount of water the more rapid the process, and as the aluminates crystalize eventually, it is better that the process take place before any considerable amount of rigidity has ensued in the cement, as there is less danger of strains being set up by the formation of crystals.

(*D*) *Regauging of Cement.*—Regauging is another process which likewise apparently affects only the aluminates. However, the results in the literature are varied, as in some cases it has been found to improve the strength of cements, and in other cases where continuous mixing has been employed the stength tests have fallen off. The effect of regauging is merely to hydrate a greater amount of aluminate than would be done by one mixing, but a very important fact is the amount of gypsum present. From this work it is very evident that the early strengths in cement are due not to the crystallization of the aluminates but to the formation of a dense, hard, amorphous mass of hydrated aluminate. Then it follows that the greater the amount of hydrated aluminate formed in 24 hours, the greater the early strength, and for this reason the high alumina cements always show high early strengths. It has already been noted that aluminates without gypsum set up almost instantaneously with water, but that a very small amount is hydrated. In other words, the grains hydrate along the edges and adhere, so that the addition of large amounts of water has little effect since it can but slowly permeate through the amorphous material which is formed. The addition of gypsum, however, allows a greater amount of water to penetrate toward the center of the grains before there is coagulation with the formation of the impermeable wall through which the water penetrates very slowly.

Manifestly, therefore, the slower setting the cement the less it will be benefited by remixing, as the effect of the latter is to mechanically remove the hydrated material from the surface of the grains, thus exposing a fresh surface to be hydrated. Conversely, a quick-setting cement will be benefited by remixing or continuous mixing, until a point is reached at which the cohesion be-

tween the hydrated particles is reduced. A cement takes up water very slowly, and if 20 per cent of water be used in mixing this is not combined even after the cement has hardened, but part of it is combined and part is mechanically held between the grains, where it slowly penetrates from the outside to the center of each grain. It is evident, therefore, that an excess of water is necessary for complete hydration. However, the greater the excess the less the cohesion between the particles of the hydrated material and the lower the resulting strength tests. Therefore, additions of gypsum to the cement and remixing the cement play the same rôle in allowing the access of water to the aluminate grains.

(*E*) *Retardation of Set Caused by Aeration.*—From the results obtained from steam tests on neat cements it has been found, as noted before, that only the aluminates and free lime were affected. The same results hold true for the aeration of cements. The slower set caused by aeration is due to the hydration of the free lime and to the absorption of a small amount of water by the aluminate grains, which thus form on their surface a thin layer of impermeable amorphous hydrated aluminate. When the cement is gauged with water, this thin layer retards the passage to the unhydrated center, a longer time ensues before hydration and coagulation takes place, and the initial set resulting from this coagulation is delayed.

(*F*) *The So-Called Abnormal Behavior in the Autoclave.*—It has been considered by several experimenters that the reactions taking place in the autoclave are abnormal and bear no relation to those taking place in normal hydration. In the considerable amount of work done with the autoclave there has been found no evidence of abnormal hydration, except in the partial dehydration of the gypsum and hydrated tricalcium aluminate. This has been overcome by filling the autoclave three-fourths full of water and immersing the briquettes, so that at all times during the test they are completely submerged in hot water. Under these conditions the crystals were very slightly altered. The aluminate crystals are very large, but no larger than those noted at the end of 28 days. On the other hand, the calcium hydroxide crystals are

much larger by the autoclave hydration than by normal hydration at 28 days. They do not lose water with the increase in temperature and pressure. By subjecting specimens to 600 pounds pressure for two hours large growths of calcium hydroxide crystals have been observed which could be removed with a pair of forceps. On the other hand, crystals of calcium hydroxide of equal size have been noted in briquettes which had been stored in sea water. The presence of salts in solution seems to favor the growth of large crystals of lime hydrate. Again, columnar aggregates growing out from the specimens have been observed in briquettes stored in fresh water for a considerable length of time. These consist of calcium carbonate evidently resulting from the carbonation of calcium hydroxide due to exposure. Wig [56] has stated that 150 pounds pressure produced the maximum strength in treated briquettes. Probably at this temperature and pressure the calcium hydroxide crystals would more nearly approximate those found by 28-day normal hardening. It has not been possible to confirm his strength tests, especially with high-silica cements, but it is found that there is an increased amount of hydrated silicate and higher strengths in briquettes at pressures much over 150 pounds. Probably his results would hold more nearly true with respect to higher alumina cements, in which the increase in temperature with increasing pressure would tend to dehydrate the aluminates.

With regard to the possible formation of a sand-lime brick bond in the specimens, as suggested by Cushman,[57] it is possible that such a reaction does take place, if there be sand present, but in the neat specimens this has never been noted. There is little, if any, uncombined silica in a normal cement which would be capable of combining with calcium hydroxide, and certainly not enough to affect the strengths in any way.

(*G*) *Action of Calcium Sulphoaluminate in Disintegration of Cement.*—Two other compounds play an important part in the hydration of cement, viz, the calcium sulphoaluminate and free lime. In considering the first compound, the disintegrating action which may accompany its crystallization has been greatly exaggerated.

[56] Eng. Record, **68**, pp. 16–17; 1913.

[57] Eng. Record, **68**, pp. 14–15; 1913.

The reason is that though the compound does crystallize with large amounts of water, the crystals produced in a hydrated cement are extremely small. Under the microscope the maximum length observed was never over 0.04 mm and the width never over 0.0025 mm, so that a suspension of the sulphoaluminate crystals has the appearance of a gelatinous precipitate. It is possible that in sea water or in alkaline water the presence of other salts in solution may assist in the development of larger crystals which might then exert an expansive force. Another fact which precludes their having any considerable disruptive action is that they begin to form simultaneously with the beginning of hydration of the aluminate, and before the cement mass has begun to assume any great rigidity.

In the disintegration of concrete by alkali, Jewett[58] has noted that failure is caused by the formation of crystals whose expansive force is enormous, but which disintegrates to a fine powder on exposure to air. The sulphoaluminate crystals probably play a part in this disintegration, although not through the expansive force of crystal growth. They form minute crystals, owing to their immediate precipitation from solution on coming in contact with limewater. These grow very little, so that any force produced must result from some other source, i. e., alkali sulphate or calcium hydroxide crystals. The sulphoaluminate crystals, however, lose water very readily and disintegrate to a fine powder. If they were present in large quantities in a cement, their drying out and disintegration would render the material very porous and readily allow the penetration of additional quantities of salt-bearing waters. Such a condition could only come about where the action of the alkali water was intermittent, allowing first a drying out and then a seepage of alkali. Framm[59] considers the presence of a small amount of sulphoaluminate crystals in cement as being beneficial, owing to the increased density which results from their presence.

(*4*) *Action of Free Lime in Accelerated Tests.*—The most interesting observations on the hydration of cements have been noted with regard to the behavior of free lime. This compound may

[58] Proc. Am. Soc. Testing Materials, 8, p. 480; 1909. [59] Chem. Ztg., 35, p. 256; 1911.

or may not be present in a cement. It is generally noted in small amounts in well-burned higher limed cements and in underburned lower limed cements. On hydration free lime will, according to its fineness, hydrate as crystalline or amorphous calcium hydroxide. It is to this formation and particularly to the growth of large calcium hydroxide crystals that the disruption observed in accelerated tests must be attributed. Kuhl [60] has noted that expansion phenomena in cement are not due to the increase in volume owing to formation of amorphous calcium hydroxide, but result from pressure caused by growing crystals and *exerted in only one plane*. Ready confirmation of this in the autoclave tests has been found.

Where the free lime is distributed evenly throughout the cement the growth of crystals may be such as to cause a briquette to expand enormously in all directions, the expansion causing a decrease in cohesion of the cement particles until complete disintegration takes place, and the briquette falls to pieces as a coarse granular powder. In other cases, where there seems to be a segregation of free lime, the development of crystals may cause cracking.

This ability of lime to form either crystalline or amorphous calcium hydroxide on hydration, depending upon the physical characteristics of the lime, readily explains the behavior of various cements in the accelerated tests. For instance, (1) some cements will not pass the boiling test, (2) some will pass the boiling test but not the autoclave test, (3) and others will pass either test after seasoning where previously they would not. In the first case the free lime is sufficiently fine and high-burned so that in the boiling test it may hydrate, crystallize, and the growth of crystals may be sufficient to cause disintegration. In the second case, the free lime may be so coarse or highly burned as not to hydrate in the boiling test, but only in the autoclave due to the high pressure and temperature employed. In the third case, aeration with insufficient water to allow solution and crystallization may cause the free lime to hydrate to the amorphous condition. In the accelerated tests there is no formation of crystals from this amorphous material, hence no disintegration.

[60] Tonind. Ztg., 36, pp. 1331–1334; 1912.

Gano [61] has noted that defective pats stored in air and water after three months stood the boiling test perfectly. In these cases the hydration of the free lime was complete, so that there was no free lime to be affected by the boiling test. These defective pats might not have passed the boiling test at either 7 or 28 days, if the hydration of the free lime were not complete, owing to the fact that hot water accelerates the hydration of unhydrated lime sufficiently to cause a rapid growth of crystals and a corresponding disruption of the other hydrated material.

It has been stated that the aluminate crystals do not grow to nearly the same extent as do the calcium hydroxide crystals. It is very probable that the falling off in strengths noted between 7 and 28 days is due quite as much to the growth of calcium hydroxide crystals as it is to the growth of hydrated tricalcium aluminate crystals.

V. SUMMARY

The following summary and conclusions are made by the authors as a result of this investigation:

This investigation included the preparation of cement minerals in conditions as nearly pure and homogeneous as possible. They consisted of the following compounds: Free lime, tricalcium aluminate, 5:3 calcium aluminate, monocalcium aluminate, beta-calcium orthosilicate, gamma-calcium orthosilicate, and tricalcium silicate. The hydrations took place on microscopic slides with an excess of water, in a cylinder with steam at atmospheric pressure, and in the autoclave with steam at various temperatures and pressures. The compounds were also molded with quantities of water approximately those used in normal-consistency mixtures. Limewater and calcium sulphate solutions were also used as the hydration medium.

With an excess of water, tricalcium aluminate hydrates as the compound $3CaO.Al_2O_3.xH_2O$, where x varies with the drying conditions. 5:3 calcium aluminate and monocalcium aluminate, on hydrating, split off amorphous hydrated alumina and form the hydrated tricalcium aluminate. Under conditions such as typified by the molded specimens, the above crystallized compound does

[61] Eng. News, **67**, p. 980.

not form immediately, but separates from solution as an amorphous material. In steam at atmospheric pressure a little crystalline aluminate is formed with the amorphous material, still more in the autoclave, and finally, on microscope slides, the hydrated tricalcium aluminate is entirely crystallized. Wherever the amorphous aluminate is formed, it slowly but eventually changes to the crystallized compound.

The hydration of the aluminates begins readily in all cases. With an excess of water the reaction progresses rapidly, and in a few days the aluminates are completely hydrated. With restricted amounts of water, however, the individual aluminate grains become coated with amorphous hydrated aluminate, through which further action proceeds with more or less difficulty.

The tests in steam at atmospheric pressure showed that the weakly basic aluminates do not absorb water above 110° C, while the more basic aluminates absorb water up to 140° C. Furthermore, a specimen of tricalcium aluminate containing high-burned free lime absorbes water even at 175° C.

The nature of the calcium hydroxide, formed by the hydration of free lime with much water, depends upon the fineness of the lime grains and the burning temperature. With coarser lime grains and with highly burned lime the hydration produces a preponderance of crystallized calcium hydroxide. On the other hand, with fine lime grains and with low-burned lime, mainly amorphous hydroxide is formed. Calcium hydroxide crystals are much more inactive chemically than the amorphous variety. White's solution, which attacks the amorphous hydroxide almost instantly, reacts extremely slowly with the crystals. In the autoclave the amorphous variety is not changed, whereas free lime yields according to its fineness and burning temperature crystallized and amorphous hydroxide. The crystals here often grow to large size, depending upon the length of time of reaction, the temperature, and the pressure.

The hydration of the aluminates in limewater reveals the same compounds as in distilled water. No new type of crystals which might indicate hydrated tetracalcium aluminate was observed. There does seem to be an action, however, between the hydrated

alumina split off and the calcium hydroxide of the solution, resulting in a greater development of crystallized hydrated tricalcium aluminate.

Aluminates hydrated in the autoclave with an excess of lime-water give no new type of compound. The plate crystals of hydrated tricalcium aluminate are rather poorly developed. The addition of dry calcium hydroxide up to 50 per cent decidedly retards the crystal growth of the aluminates in the autoclave.

The first effect of gypsum solution on the aluminates is to retard the formation of amorphous hydrated material and keep the pores of the material open to the further penetration of water. Specimens hydrated in saturated gypsum solutions show the highest ignition loss after six days. The products of hydration are the same as those with distilled water, with the exception of the additional formation of sulphoaluminate needles. This new compound is identical for all three aluminates, and its formula is $3CaO.Al_2O_3$, $3CaSO_4$, xH_2O. The formation of this compound is only incidental to the initial set and not the cause of its retardation, since the compound is formed before, during, and after the set. Variation of the gypsum content above and below a certain definite concentration causes a decrease in the setting time.

The problem of initial set is probably one involving the action of small amounts of electrolytes in retarding the coagulation of the amorphous aluminate material. The evidence is in favor of the fact that the aluminates coagulate and separate as amorphous bodies from supersaturated solutions, the rate of coagulation being affected by such small quantities of electrolyte as to preclude the possibility of the reaction being solely a chemical one. Thus with a certain and definite concentration of gypsum, maximum hydration is attained, and at the same time the rate of coagulation is retarded, increasing the time of set.

The sulphoaluminate crystals are broken up in the autoclave, as is also gypsum. Club-shaped crystals are noted with optical constants that suggest a composition between gypsum and anhydrite. With higher temperatures and pressures water is even driven out of the amorphous hydrated aluminate. Gypsum favors the growth of hydrated tricalcium aluminate crystals in the autoclave.

Calcium metasilicate, as well as gamma-calcium orthosilicate, is practically inert with regard to hydration. Beta-calcium orthosilicate is but slightly hydrated in water after a considerable length of time. This is manifested by a slight etching of the grains and the formation of a small amount of amorphous material. The action of limewater and plaster solution does not materially increase the hydration. The treatment of this silicate with tricalcium aluminate solution gives maximum hydration and the best 28-day test pieces. In mixtures of the beta-orthosilicate and the aluminates the latter show some hydration while the former is unhydrated after 24 hours, at which time cements are exposed to accelerated tests. At 28 days the aluminates are completely hydrated, and the silicate shows quite a little hydration. The test pieces, while exhibiting fairly good rigidity, have not the strength of corresponding cement briquettes. The slides of beta-calcium orthosilicate and aluminates indicate that the hydration of the aluminates proceeds as previously noted. With an excess of water the silicate hydrates more quickly than with limited water, the product being the same amorphous gel-like material.

Homogeneous tricalcium silicate was not obtained, the most satisfactory product containing an extremely small amount of free lime, beta-orthosilicate and tricalcium aluminate. Tricalcium silicate acts entirely differently from either beta-orthosilicate or mixtures of beta-orthosilicate and lime, with respect to hydration. It hydrates readily with excess of water, with limited water, and in the autoclave. The products of hydration are identical and consist of calcium hydroxide crystals and amorphous hydrated silicate. No hydrated calcium metasilicate needles are observed. It sets hard in 5 hours and shows no sign of disintegration after 28 days in water, in the autoclave. The size of the calcium hydroxide crystals depends upon the pressure. In general the greater the pressure the larger the crystals. Mixing tricalcium silicate with beta-calcium orthosilicate has no favorable effect on the hydration of the latter.

Mixtures of tricalcium silicate and the aluminates gauged with water, lime water, and plaster solution show first the beginning of hydration of the aluminate, followed shortly by the hydration of

the silicate. The 28 specimens are extremely dense, hard, and strong, comparing very favorably with the strongest neat cement briquets.

The hydration of cements is thus brought about by the formation of amorphous hydrated tricalcium aluminate with or without amorphous alumina, the aluminate later crystallizing. At the same time sulphoaluminate crystals are formed, and low-burned or finely ground lime is hydrated. The formation of the above compounds begins within a short time after the cement is gauged. The next compound to react is tricalcium silicate. Its hydration may begin within 24 hours, and it is generally completed within 7 days. Between 7 and 28 days the amorphous aluminate commences to crystallize and beta-orthosilicate begins to hydrate. Although the latter is the chief constituent of the American Portland cements, it is the least reactive compound. The early strength (24 hours) of cements is probably due to the hydration of free lime and the aluminates. The increase in strength between 24 hours and 7 days depends upon the hydration of tricalcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between 7 and 28 days is due to the hydration of beta-calcium orthosilicate, but here are encountered opposing forces, in the hydration of any high-burned free lime present and in the crystallization of the aluminate. It is to this hydration that the falling off in strength between 7 and 28 days of very high-burned high limed cements is due, whereas the decrease shown by the high alumina cements is due to the crystallization of the aluminate. Finally, the iron in the cement is resistive to hydration and does not form any definite crystalline hydration products, but occurs as a rust-like material.

The last statement is perfectly true for the *cements we have examined* and contains nothing derogatory to the so-called iron cements.

WASHINGTON, April 18, 1914.

TABLE 1

Showing Hydration of Aluminates

		Slides	Steam at atmospheric pressure	Autoclave.	Molded specimens
Tricalcium aluminate.	With water....	Needles and hexagonal plates of hydrated tricalcium aluminate. No amorphous material.	Absorbs water to 140°. Needles, crystals, and a few plates. A little amorphous material, also unhydrated tricalcium aluminate.	Considerable amorphous material, a few needles, and plates. No unhydrated material.	Hydration product after 24 hours entirely amorphous, grains showing unhydrated centers and hydrated edges.
	With limewater.	Same constituents as with water. No new type of crystals denoting hydrated tetracalcium aluminate.	No tests made.....	With limewater products same as above with greater number of plate crystals. With dry calcium hydrate crystallization is retarded and amount of amorphous hydrated aluminate is increased.	7-day specimens still contain a few unhydrated grains. Hydrated material is mainly amorphous with a few small plates and needles; 28-day specimens are completely hydrated and show increase in needles and plates.
	With plaster solution.	Crystals of hydrated tricalcium aluminate formed together with extremely fine needles of calcium sulphoaluminate.	.....do.....	Sulphoaluminate crystals destroyed. Club crystals noted with optical properties denoting a composition between gypsum and anhydrite. Also large needles and plates of hydrated tricalcium aluminate and amorphous material.	7-day specimens show very little unhydrated aluminate. Hydration products are both crystalline and amorphous hydrated tricalcium aluminate and calcium sulphoaluminate crystals.
5:3 calcium aluminate.	With water....	Needles, plates, and radial spherulites of hydrated tricalcium aluminate and some amorphous material (hydrated alumina).	Absorbs water to 140°. Splits off hydrated alumina and forms hydrated tricalcium aluminate. Considerable unhydrated aluminate.	Amorphous material, plates and lath-shaped crystals of hydrated tricalcium aluminate. No unhydrated material.	After 24 hours chiefly amorphous material, very little crystal development. Unhydrated centers.
	With limewater.	.....do.....	No tests made.....	With limewater product same as above. With solid calcium hydrate crystallization is retarded and amorphous material increased.	7-day specimens contain a little unhydrated aluminate, also amorphous material and a few hydrated tricalcium aluminate crystals; 28-day speci-

					mens are completely hydrated and show considerable increase in needles and plates.
	With plaster solution.	Hydration products are crystals of hydrated tricalcium aluminate, amorphous hydrated alumina and sulphoaluminate crystals.	.....do.....	Sulphoaluminate crystals destroyed. Quite a quantity of hydrated tricalcium aluminate crystals noted. Amorphous material and club-shaped crystals of $CaSO_4.xH_2O$.	7-day specimens show a little unhydrated material. Hydration products are crystallized hydrated tricalcium aluminate and amorphous hydrated material, also sulphoaluminate.
	With water....	Crystallized material consists of needles, plates, and spherulites of hydrated tricalcium aluminate. Also considerable amorphous hydrated alumina.	Absorbs water to 110° with formation of amorphous hydrated alumina crystalline hydrated tricalcium aluminate. Considerable unhydrated material noted.	Considerable amorphous material, also needles and plates of hydrated tricalcium aluminate.	Hydration product after 24 hours almost entirely amorphous, with few needle crystals.
Monocalcium aluminate.	With lime-water.	.....do.....	No tests made.....	With limewater same products as with water. Solid calcium hydrate up to 50 per cent favors the formation of amorphous hydrated material.	7-day specimens contain a little unhydrated material, much amorphous material, and quite considerable crystallized hydrated tricalcium aluminate in greater amount than in corresponding water specimen; 28-day specimens contain no unhydrated material.
	With plaster solution.	Crystals of hydrated tricalcium aluminate. Considerable amorphous hydrated alumina and well-developed crystals of calcium sulphoaluminate.	.....do.....	Contains a few hydrated tricalcium aluminate crystals, considerable amorphous material, and club-shaped crystals.	7-day specimens are all hydrated and consist of amorphous material, needles, and plates of hydrated tricalcium aluminate, also calcium sulphoaluminate crystals.

TABLE 2

Showing Hydration of Silicates

		Slides	Steam at atmospheric pressure	Autoclave	Molded specimens
Calcium metasilicate.	With water	No hydration	No hydration	Extremely slight etching	No hydration.
	With lime-water.	do	No tests	No tests	No tests.
	With plaster solution.	do	do	do	Do.
Gamma-calcium orthosilicate.	With water	do	Extremely slight hydration (0.52 per cent water absorbed).	Trace of hydration	No hydration.
	With lime-water.	do	No tests	No tests	No tests.
	With plaster solution.	do	do	do	Do.
Beta-calcium orthosilicate.	With water	No hydration until after considerable length of time.	No hydration	Slight etching and formation of minute quantity of amorphous material.	No hydration.
	With lime-water.	Practically not different from specimens in water.	do	do	28-day specimens consist almost entirely of unhydrated beta-orthosilicate with a little amorphous material.
	With plaster solution.	do	do	do	Do.
	With tricalcium aluminate solution.	No tests	No tests	No tests	28-day specimens show much greater hydration of orthosilicate with formation of amorphous hydrated material, but no calcium hydroxide. Beta-orthosilicate shaken with large excess of solution for 10 days shows maximum hydration and ignition loss of 4.04 per cent.

Tricalcium silicate.	With water....	Started to hydrate within 24 hours with formation of crystals of calcium hydroxide and amorphous hydrated silicate. After three weeks hydration the slide was covered with amorphous material.	A slight amount of water absorbed at 140 and up to 200°, due to hydration of free lime present.	Hydration products are amorphous hydrated calcium silicate and crystals of calcium hydroxide whose size increase with increase in pressure. Completely hydrated.	Specimens with 20 per cent water set hard at the end of five hours showed no disintegration after 28 days. Hydration products are amorphous hydrated calcium silicate and crystallized calcium hydroxide.
	With lime-water.	.....do.....	No tests made.....	No tests made.....	No tests made.
	With plaster solution.	.....do.....	.....do.....	Products are the same as with tricalcium silicate hydrated in the autoclave with water except for the additional formation of $CaSO_4.xH_2O$.	Specimens with 20 per cent plaster solution set up hard and showed no disintegration at end of 28 days. Hydration products same as with hydration in water.
Tricalcium silicate and beta-calcium orthosilicate with plaster.	.....	.....	.....	Trisilicate completely hydrated. Orthosilicate very slightly hydrated.	

TABLE 3

Showing Hydration of Silicates and Aluminates

		Slides	Steam at atmospheric pressure	Autoclave	Molded specimens
Calcium metasilicate and aluminates.	With water	Aluminates hydrate to usual products. Silicate entirely unhydrated.	No tests made	No tests made	No tests made.
	With limewater.	do	do	do	Do.
	With plaster solution.	do	do	do	Do.
Gamma-calcium orthosilicate and aluminates.	With water	Aluminates hydrate as usual, but silicate is entirely resistant.	do	do	Do.
	With limewater.	do	do	do	Do.
	With plaster solution.	do	do	do	Do.
Beta-calcium orthosilicate and aluminates.	With water	Aluminates began to hydrate first to usual hydration products. Silicate began to be etched in less than a week, and amorphous hydrated silicate was formed. At end of three weeks silicate covered the whole slide.	Aluminates hydrated to quite an extent. Silicate unhydrated.	Aluminates hydrated. Orthosilicate but slightly etched.	28-day specimens somewhat friable. Aluminates hydrated entirely to usual hydration products. Silicate hydrated to quite an extent.

	With lime-water.	.....do.....	No tests made.....	No tests made.....	Same as with water, with a slight increase in amount of hydrated material.
	With plaster solution.	Same as with water, with the additional formation of calcium sulphoaluminate crystals.	.....do.....	Same as with water, but for the additional formation of $CaSO_4.xH_2O$ crystals.	Same as with water, with the formation of sulphoaluminate needles.
Tricalcium silicate and aluminates.	With water....	Aluminates began to hydrate first. Trisilicate started to hydrate within 24 hours to calcium hydroxide and amorphous hydrated silicate. The latter covered slide in a week.	Aluminates hydrated to quite an extent. Trisilicate slightly hydrated.	Both silicate and aluminate hydrated. Calcium hydroxide crystals grow to large size.	28-day specimens hard and compact. Show complete hydration of silicate and aluminate. Amorphous aluminate has begun to crystallize. Amorphous hydrated silicate noted, also calcium hydroxide crystals.
	With lime-water.	.....do.....	No tests made.....	No tests made.....	Same as with water.
	With plaster solution.	Same as with water, with the additional formation of sulphoaluminate crystals.	.....do.....	Same as with water, but with the additional formation of $CaSO_4.xH_2O$ crystals.	Same as with water, with the additional formation of sulphoaluminate crystals.

TABLE 4

Showing Hydration of Cements

	No. 1	No. 2	No. 3	No. 4
24 hours..	No calcium hydroxide crystals, a little isotropic amorphous hydrate. Tricalcium silicate very slightly hydrated. Orthosilicate unhydrated. Aluminate considerably hydrated to amorphous material. No needles or plates present.	Some amorphous calcium hydroxide. No crystals. Amorphous hydrated trialuminate; trisilicate slightly hydrated. Orthosilicate unchanged.	Very little amorphous calcium hydroxide. Aluminate hydrated to amorphous material. Trisilicate and orthosilicate unhydrated.	A few small calcium hydroxide crystals with some amorphous hydrate. Trisilicate hydrated a little. Orthosilicate unhydrated. Trialuminate nearly all hydrated to amorphous material.
7 days....	A large number of calcium hydroxide crystals and some amorphous hydrate. Trisilicate all hydrated. Orthosilicate slightly hydrated. Aluminate all hydrated to amorphous material with a few needles and plates.	Calcium hydroxide crystals not as well developed as in No. 1 (seven days); amorphous hydroxide. Trisilicate almost all hydrated. Aluminate hydrated to a few needles and plates and much amorphous material.	Calcium hydroxide crystallized and small amounts of amorphous hydroxide noted. Trisilicate all hydrated. Orthosilicate very slightly hydrated. Aluminate hydrated to amorphous material with a few needles and plates.	Calcium hydroxide crystals large and more plentiful than in No. 4 (24-hours sample). Amorphous hydroxide. Trisilicate all hydrated. Orthosilicate slightly hydrated. Hydrated aluminate consisted of amorphous material with some needles and plates.
28 days...	Large amount of calcium hydroxide crystals and some amorphous hydroxide. Trisilicate all hydrated. Orthosilicate considerably hydrated, the hydrated silicate product in both cases being amorphous. Aluminate nearly all in fine needles and plates, a smaller amount being still amorphous.	Large crystals of calcium hydroxide. Some amorphous calcium hydroxide. Trisilicate all hydrated. Orthosilicate not very greatly hydrated. Hydrated aluminate needles and small plates rather plentiful.	Plenty of calcium hydroxide crystals and a little amorphous hydroxide. Trisilicate all hydrated. Orthosilicate partly hydrated and surrounded by amorphous material. Trialuminate present as needles, plates, and amorphous material.	A large number of calcium hydroxide crystals and some amorphous hydroxide. Trisilicate all hydrated. Quite a little orthosilicate still unhydrated. Aluminate as needles, plates, and amorphous material. Iron material slightly hydrated to opaque material being reddish and resembling iron rust.

Autoclave after 24 hours in damp closet.	Very large calcium hydroxide crystals and some amorphous hydroxide. Trisilicate all hydrated. Orthosilicate considerably hydrated. Aluminate all hydrated to amorphous material and needles.	Large calcium hydroxide crystals, some amorphous hydroxide. Trisilicate hydrated. Orthosilicate but slightly hydrated. Trialuminate all hydrated to amorphous material and needles.	Calcium hydroxide crystals larger than any of the others. Some amorphous hydroxide. Trisilicate hydrated. Orthosilicate partially hydrated. Trialuminate hydrated to amorphous material and needles.	Large calcium hydroxide crystals, some amorphous hydroxide. Trisilicate all hydrated. Much orthosilicate still unhydrated. Hydrated trialuminate needles and amorphous material observed. Iron material hydrated to reddish opaque fine-grained product.

NOTE.—Sulphoaluminate crystals observed in all specimens except those in the autoclave, where they are destroyed and $CaSO_4.\times H_2O$ formed.

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No. 44

INVESTIGATION OF THE DURABILITY OF CEMENT DRAIN TILE IN ALKALI SOILS

(CONTAINING RESULTS OF FIRST YEAR'S TESTS)

By

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INVESTIGATION OF THE DURABILITY OF CEMENT DRAIN TILE IN ALKALI SOILS

By R. J. Wig and G. M. Williams,

In cooperation with S. H. McCrory, E. C. Bebb, and L. R. Ferguson

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I. INTRODUCTION

The disintegration of concrete when exposed to strongly alkaline soils and waters in arid regions of the western part of the United States has been a subject of discussion by engineers and users of cement for the past 10 or 15 years. There are many concrete

structures in these districts which do not appear to be affected by the salts, but there are some which were apparently made of good materials and were well fabricated which show indications of being attacked.

There are many engineers who believe that well-fabricated concrete will not disintegrate when exposed to these alkali salts and that many cases of failure which have been reported have not been caused primarily by the alkali but resulted from the use of poor aggregate, improper methods of fabrication, or other causes which resulted in a poor quality of concrete.

A laboratory investigation was started in 1908 by the technologic branch of the United States Geological Survey to determine the effect of alkali waters on cements and concretes. In 1910 this work was transferred, by act of Congress, with all structural materials investigations, to the Bureau of Standards. The investigations were continued and the results were published in 1912.[1] Briefly, these investigations showed that practically all cements are attacked by alkali waters upon exposure in the laboratory, and complete disintegration can be obtained under certain conditions. Similar investigations have been made by other laboratories with similar results.[2]

Disintegration in the laboratory can apparently be obtained in two ways. If the cement specimen is somewhat porous and it is constantly supplied with a salt solution which is permitted to crystallize in the pores, disintegration may result from the mechanical force exerted. If hydrated cement is brought into intimate contact with certain sulphate or chloride solutions, the uncarbonated lime of the cement is subject to comparatively rapid solution, with a resulting decomposition of the cement. Laboratory tests, however, must always be interpreted with caution, as conditions often differ somewhat from service, and it is on this account that a field investigation was undertaken in which cement mortar and concrete mixtures of various qualities could be brought into intimate contact with alkali salts under natural conditions.

The Bureau of Standards has made a field survey of concrete structures exposed to alkali waters in several of the Western

[1] Technologic Paper No. 12, "Action of the salts in alkali water and sea water on cements."

[2] Montana State Agricultural College, Circular No. 8, 1910; Bulletin No. 81, 1910. Colorado Agricultural Experimental Station, Bulletin No. 132.

States. There is a tendency for the cement user to attribute to alkali all failures occurring in these districts, if any alkali is visible in the surrounding soil. Therefore, such failures as occur in the eastern part of the United States, due to poor materials or improper methods of fabrication, are often excused in the irrigated districts as failures due to alkali.

A description of several of the structures which were examined will serve to illustrate the conditions as they exist.

In Fig. 1 is shown a small concrete structure known as a "turn-out" for irrigation water, which was built about 1907. One portion of this structure is completely disintegrated while another portion is sound. The sound portion is a beam on the lower side extending into the wing walls exposed to the earth at each end and located so that half of it is above the concentrated alkali water and half below. The composition of the salts was found to be as follows:

	Per cent
Water soluble	65.33
Insoluble	31.19
Loss at 110° C	3.14

Analysis of water soluble portion:

	Per cent
CaO	0.04
MgO	.38
Na_2O	43.60
K_2O	.11
SO_3	53.58
CO_2	2.19
Cl	.77

The following method was used for determining the water soluble portion:

Five grams of the sample were heated to 110° C for 18 hours or until constant weight was obtained. This gave "loss at 110° C." This dried residue was digested with 50 cc of water, filtered and washed until practically free from salts soluble in water. The "insoluble" was dried at 110° C and weighed. Aliquot parts of the solution were taken for determination of soluble salts.

The form marks were still visible on the beam when examined in 1912, and it did not appear to have been affected in the least by the alkali salts. The remainder of the structure is completely disintegrated so that it can be torn apart with the hands and the

pores are filled with salts. This canal has never been used for the purpose of distributing irrigation water, and the structure is exposed to the concentrated seepage water which collects from the higher surrounding land and which flows through the ditch.

The beam was molded and cured in the yard and set into place in the "turnout" several days later, at the time the turnout was cast. No records were available to show the composition or method of molding, but it was stated that probably the same materials and proportions were used in both parts of the structure. The primary cause of failure of the disintegrated portion may not be the alkali salts, although it would appear that alkali might be responsible. The excellent condition of the beam, however, would demonstrate that concrete can be made which will resist, at least for a number of years, the action of concentrated alkali of the character found at this locality.

Fig. 2 shows the lower end of a small concrete gate culvert, which is badly disintegrated. Alkali salts are visible on the surface of the soil surrounding the culvert at the lower end. The water carried through the culvert is fresh irrigation water. The walls of the culvert at the upper end appear sound and normal. An analysis of the disintegrated concrete taken from the walls at the lower end give the following results. Two analyses were made of the sample, (a) of the solid lumps, (b) of the soft or crumbly portion.

	(a)	(b)
	Per cent	Per cent
Insoluble: Sand, etc	79.26	65.80
Soluble:		
SiO_2	3.29	3.60
Fe_2O_3	1.20	.80
Al_2O_3	1.57	2.06
CaO	7.02	13.64
MgO	.60	.55
SO_3	.14	.25
Cl	Trace.	Trace.
CO_2	4.67	8.82
Water, etc., at 500° C	2.18	4.39

The foregoing analyses computed to a "sand and moisture free" basis give:

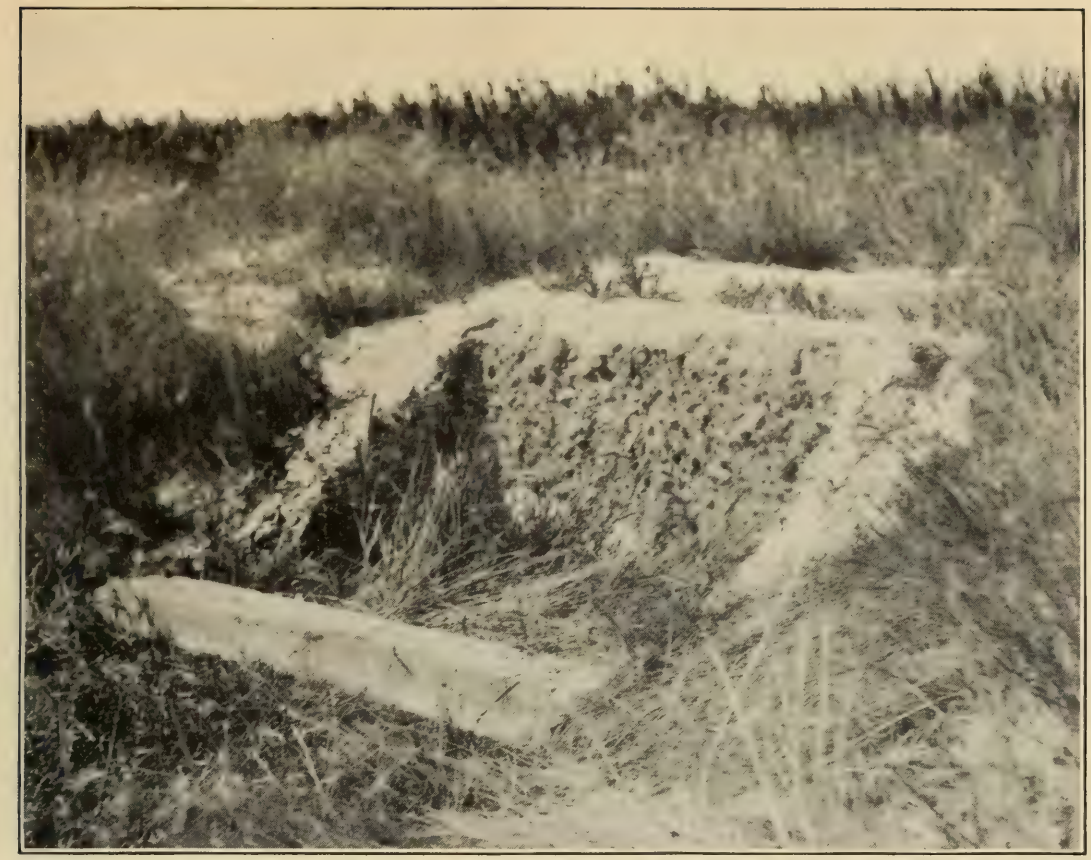

FIG. 1.—*Concrete "turnout" in alkali soil on abandoned irrigation canal, showing the complete disintegration of one portion of the structure, with a premolded beam in the foreground which is perfectly sound. White appearance of disintegrated portion is caused by the alkali salts which fill the pores*

FIG. 2.—*Concrete gate culvert in alkali soil on irrigation canal. Note complete disintegration of concrete in foreground while upper end is perfectly sound. White deposit of alkali is visible on the left above the surface of the water*

	(a)	(b)
Soluble:	Per cent	Per cent
SiO	17.80	12.12
Fe_2O_3	6.49	2.69
Al_2O_3	8.50	6.93
CaO	37.98	45.90
MgO	3.25	1.85
SO_3	.76	.84
CO_2	25.22	29.67

After calculating the amount of MgO and CaO necessary to satisfy the CO_2 and SO_3 there is left in (a) 9.8 per cent CaO and in (b) 10.1 per cent CaO.

These analyses show no abnormality which would account for the disintegration. The sodium and potassium were not determined, but they were evidently not in excess of 1 per cent. The SO_3, Cl, and MgO were also normal. Therefore it would seem that the failure could not have been caused by the alkali, although no other explanation can be offered without a knowledge of the materials used, method employed, and weather conditions at the time of fabrication. This information is not available.

The concrete wing wall of a large culvert shown in Fig. 3 was cited as a case of disintegration due to alkali salts. Upon investigation it was found that there was a bend in the creek at the point where the culvert is located, and during flood the creek carried bowlders 12 to 20 inches in diameter which would be thrown against the wall.

Alkali salts are visible in the pores where the surface is eroded to a considerable depth, but the cement and concrete appears hard and the presence of the alkali would seem to be incidental and contributory rather than the initial cause of disintegration. The composition of the alkali salts taken from the surface was as follows:

Soluble (calculated on 100 per cent basis):	Per cent
CaO	0.91
MgO	.48
Na_2O	41.32
K_2O	Trace.
SO_3	55.98
Cl	.16
CO_2	Trace.

In Fig. 4 is shown a large railroad culvert with a portion of an old concrete structure remaining in the foreground. The concrete remaining from the old structure is completely disintegrated, so that it can be torn apart with the fingers, and alkali salts are found in the pores. The new culvert, which is about eight years old, appears to be sound and normal with the exception of a few spots near the ground line which can be scraped away with a knife. The culvert as a whole does not evidence good workmanship in fabrication.

The surface of the surrounding soil is covered with alkali salts having the following composition:

	Per cent
Water soluble	8.45
Insoluble	78.35
Loss at 110° C	13.98

Analysis of water soluble portion:	Per cent
CaO	36.16
MgO	.71
Na_2O	5.37
K_2O	.24
SO_3	57.28
Cl	.24

In Fig. 5 is shown a small concrete retaining wall the coping of which is disintegrated and referred to as a failure due to alkali salts. The surface of the soil surrounding this wall, both at the top and along the sides, shows the presence of alkali salts. The wall is sound and hard at all points examined excepting the coping where disintegration is shown. Since structures are found in the East where no alkali salts are present, which appear just as the one shown with the coping sluffed off due to frost action on a very weak section in the concrete that results from the use of watery mixtures, it is quite possible that the disintegration of the coping in this structure is due to that cause. In mixtures in which an excessive amount of water is used the fine material in the aggregate and cement will float to the surface in the forms as they are filled and collect at the top of the form, resulting in a very porous and weak section which is readily attacked by frost.

It is practically impossible to analyze some of the failures which have occurred and state definitely the part played by the alkali salts, as a result of which it was deemed desirable to make field

FIG. 3.—*Concrete wing wall of culvert in alkali soil under irrigation canal. Damage attributed to alkali due to appearance of alkali on eroded surface. Initial erosion probably due to impact of large bowlders brought down by flood water*

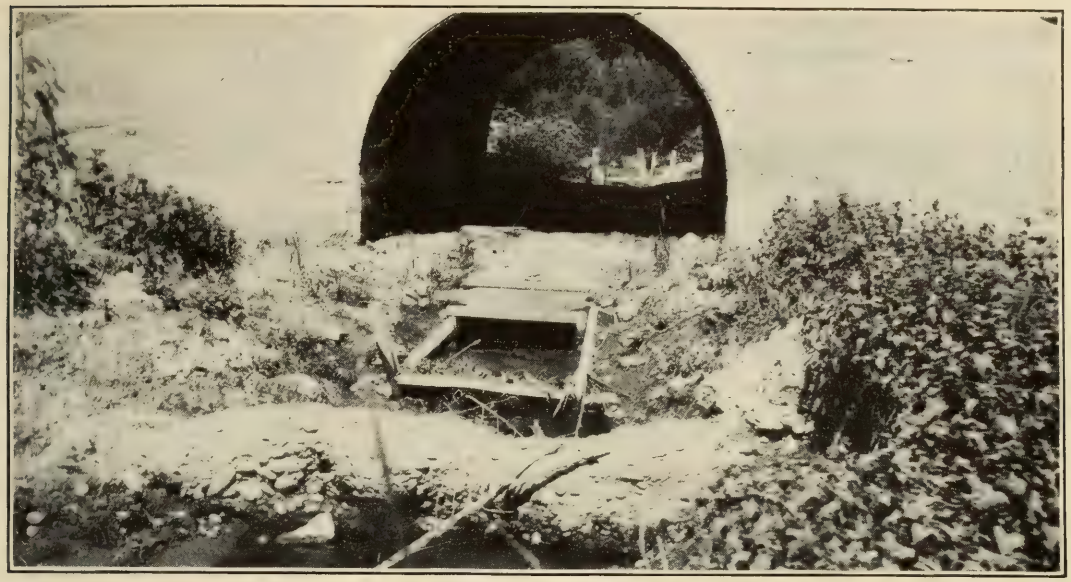

FIG. 4.—*Concrete culvert in alkali soil under railway roadbed. Small mass of concrete in foreground remaining from an earlier structure is completely disintegrated. Present structure shows no effect of alkali action although it is considerably cracked from settlement*

FIG. 5.—*Concrete retaining wall in alkali soil. Alkali salts are visible in the surrounding soil. There is no disintegration of concrete in lower section just above water level, where it usually occurs. Disintegrated coping is probably due to use of excess of water in concrete at time of placing*

tests in which concrete of known composition and fabrication would be exposed in some of the worst known alkali districts in the West.

It was decided that this investigation should be started by exposing various cement mixtures in the form of drain tile, because of its economic importance. It will probably become necessary to drain the greater part of all lands under irrigation, and much of this drainage will require the use of tile. The cost of drainage has been estimated as approximately $25 per acre, from which it is seen that many millions of dollars must be spent for this purpose. At the present time there are few known deposits of clay available for the manufacture of satisfactory clay tile in these districts, while materials for the manufacture of cement tile are usually found close at hand, but many engineers are skeptical of the permanency of cement tile, as a number of failures have occurred which have been reported to have been caused by the alkali salts.

This investigation of cement tile should be followed with an exposure of generous sized blocks of concrete of known composition which would simulate mass construction and would extend from below the surface of the ground or water, in order to determine the possibility of disintegration by the mechanical force exerted by the crystallization of the salts absorbed by capillarity into the pores of the concrete above the water or ground surface. It is anticipated that such an investigation will be conducted.

It is desired to thank the United States Reclamation Service and the several project managers and engineers for their assistance and for furnishing the labor necessary in installing the drains at Montrose, Colo.; Garland, Wyo.; Fort Shaw, Mont.; Sunnyside, Wash.; and Yuma, Ariz.; the drainage division of the Department of Agriculture and their field engineers for their assistance and for furnishing the labor necessary in installing the drains at Grand Junction, Colo.; Columbia, Mo.; Crookston, Minn.; Huntington, Utah; and Roswell, N. Mex.; the Iowa State College for providing storage space for a complete set of tile; and P. H. Atwood and the Armstrong Cement Works, Armstrong, Iowa, for their hearty cooperation and interest in the manufacture of the tile. Acknowledgment is also made to the chemical division, A. N. Finn, and

G. J. Hough, of the Bureau of Standards, for the chemical analyses of waters, alkalies, soils, and disintegrated concretes.

II. OUTLINE OF INVESTIGATION

An advisory committee was organized composed of S. H. McCrory, chief of drainage investigations, Department of Agriculture; F. W. Hanna, supervising engineer of the United States Reclamation Service (later succeeded by E. C. Bebb, engineer, Reclamation Service); L. R. Ferguson, assistant secretary of the Association of American Portland Cement Manufacturers; and Rudolph J. Wig, of the Bureau of Standards. This committee held several meetings and finally developed a program which required the manufacture of about 8800 cement drain tile made up of 16 different varieties, as shown in the schedule below.

Schedule of Mixtures and Processes of Manufacture of the Tile

Series	Proportions cement-sand	Consistency	Manufacture	Curing
1	1:2½	Plastic	Handmade	Sprinkling
2	1:2½	Quaking	do	Do.
3	1:2	Plastic	do	Steam
4[a]	1:2	do	do	Do.
5[b]	1:2	do	do	Do.
6[c]	1:2	do	do	Do.
7	1:3	do	Machine-made	Do.
8	1:4	do	do	Do.
9	1:1½	do	do	Sprinkling
10	1:1½	do	do	Steam
11	1:3	do	do	Sprinkling
12	1:4	do	do	Do.
13	1:2½	do	do	Steam
14	1:3	Fluid	Handmade	Sprinkling
15[d]	1:3	do	do	Do.
16[e]	1:4	Plastic	Machine-made	Steam

[a] Dipped in neat cement grout, 20 to 24 hours after molding.
[b] Dipped in hot tar 6 weeks after molding.
[c] 10 % ferrous sulphate, by weight, added to mixed water.
[d] Sand-cement used in place of Portland cement.
[e] From factory stock pile. Northwestern States Portland cement. Age probably 6 months when above series were made.

The tile were made as described later, under contract at a commercial tile plant, and under the supervision of a representative of the Bureau of Standards. Work was commenced in July and

completed in September, 1913, and shipments were made in October, which allowed a curing period of one month for the last tile made. Although it was anticipated that some of the tile of the leaner mixtures which are satisfactory in the humid regions would fail in these alkali soils, the program was arranged to include tile made from the leanest to the richest commercial mixtures.

The tile were installed in operating drains on eight projects in the most concentrated alkali soils available in the West and on projects where there was practically no alkali for comparison. The location of these projects is as follows:

Alkali projects: Garland, Wyo.; Fort Shaw, Mont.; Huntington, Utah; Sunnyside, Wash.; Yuma, Ariz.; Roswell, N. Mex.; Grand Junction, Colo.; Montrose, Colo.

Fresh-water projects: Crookston, Minn.; Columbia, Mo.

One set of tile of each type also was stored in the open exposed to the atmosphere at Ames, Iowa, for reference and test.

The program requires the removal of at least two tile of each type at each project every year for test and inspection. Sufficient tile were made and installed to continue the investigation 10 years or longer if necessary.

To replace the tile which were removed for test during 1914 a supply of 8-inch cement tile were furnished by the Universal Portland Cement Co. A description of the materials and methods used for the manufacture of these tile is included under the heading "Manufacture of drain tile." A group of each of these series, numbered 17 and 18, will be removed in 1915 when the second year's tests will be made.

Tile removed for test during 1915 will be replaced by cement tile furnished by the Utah Concrete Pipe Co., Salt Lake City, Utah.

III. MANUFACTURE OF DRAINTILE

1. FACTORY AND EQUIPMENT

The cement test pieces used in this investigation were made at the tile plant of the Armstrong Cement Works, Armstrong, Iowa. This factory has for a number of years been producing large quantities of cement tile, varying in size from 4 to 30 inches, for use in northern Iowa.

The factory building consists of a concrete block and frame structure, which houses the mixers and tile-making machines, with a large low-roofed concrete block addition to one side, which is divided into curing chambers. A railroad switch used for the delivery of materials and shipment of the finished product parallels the building on the opposite side.

Sand is received in dump-bottom coal cars and dropped into a pit, from which it is drawn by a chain drag to the foot of a bucket elevator. After being elevated the sand is dropped into either of two storage bins, or is carried overhead on a belt directly to a sand-storage box, placed above the hopper of a batch mixer. In making commercial tile this hopper is filled with sand to a fixed height, depending upon the proportions desired, and the cement is added. The gate is then opened and the material passes into the batch mixer, which consists of a cylindrical steel drum mounted on rollers. The interior of the mixer contains scoops or buckets, which carry the material up and drop it during rotation. This mixer is very satisfactory in use, mixing the sand and cement uniformly and quickly, but the time required varies considerably, due to the varying amounts of moisture in the sand. A very damp sand generally requires two or three times as many revolutions of the mixer as does a dry sand.

After the cement and sand are thoroughly mixed dry the mass is dropped into another hopper just above a continuous mixer or pug mill. (See Fig. 6.) As the dry material is fed into the upper end of the trough of the pug mill, water is sprayed in through a perforated pipe, the amount being regulated by the man at the mixer. To obtain a uniform mixture an experienced man is required, as the rate of feed of the material and the amount of moisture in the sand vary constantly.

This factory is equipped with several tile machines, the Schenck being used in making all the experimental machine-made tile. This machine is of the revolving packer type, the tile being formed between the stationary metal jacket and the packer, which is drawn upward and out of the tile as it revolves.

The car system is in use for handling the smaller sizes of tile after molding. The equipment consists of a suitable number of

FIG. 6.—*Combination batch mixer and pug mill. Materials are thoroughly mixed dry in cylindrical steel drum, then dropped into hopper above pug mill into which the dry mixture flows in a small continuous stream. Water is added through a perforated pipe as the materials are forced through the horizontal trough by the rotating blades*

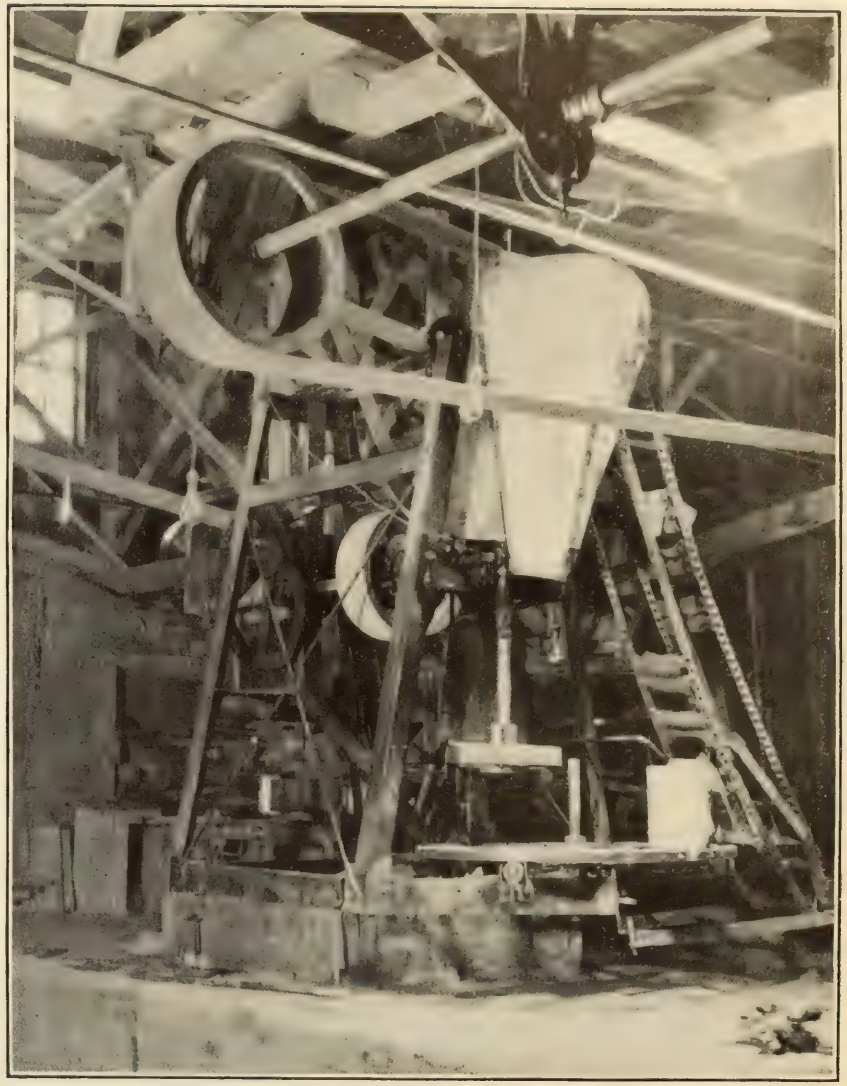

FIG. 7.—*Schenck cement tile machine. When the packer head on the vertical rotating shaft is in its lowest position cement mortar is automatically dumped into the mold by a bucket elevator and the material is packed against the wall of the mold by the rotating packer head as it is withdrawn vertically*

three-deck cars equipped with springs and roller bearings, transfer trucks, and trackage into the curing chambers and out to the various points in the storage yard.

Steam curing of concrete products is used exclusively for curing the regular output of this factory, but all rooms are equipped with water pipes for sprinkling the product, which was the method desired for several of the series of our experimental tile. Cars containing small tile are pushed into low-roofed block-walled rooms, about 90 feet long, holding 11 cars, with enough clearance on one side to allow a man to pass along the cars and sprinkle the tile. Large tile, wheeled on carts, are cured in two large rooms having concrete floors. Exhaust steam from the engine of an electric lighting plant, owned by the same company, is piped to the various rooms and utilized for curing. Steam was available 16 hours per day.

2. MATERIALS

The cement used in this work was Hawkeye brand Portland cement, supplied under contract by the Iowa Portland Cement Co., Des Moines, Iowa. Approximately 240 barrels of Portland cement were required. For the manufacture of series 15, a sand cement was supplied by the United States Reclamation Service, from the sand-cement mill in operation at Arrowrock, Idaho. The results of chemical and physical tests of the cements are given in Table 1.

The sand used was shipped in from Mason City, Iowa, being the material regularly used in the factory.

Analysis and tests of sand are shown in Table 2. The water was pumped from a well at the factory. Power was furnished to the entire equipment by a 20-horsepower electric motor, receiving current from the electric lighting plant.

3. MACHINE-MADE TILE

These tile made on the Schenck cement tile machine (Fig. 7) are 12¼ inches in length, three-fourths inch thick, with an inside diameter of 8 inches.

TABLE 1

Results of Tests of Cement Used in Manufacture of Cement Drain Tile

HAWKEYE PORTLAND CEMENT

Sample	Specific gravity	Fineness		Time setting		Soundness		
		100-mesh	200-mesh	Initial	Final	A	W	S
		Per cent	Per cent					
1	3.16	94.0	77.8	5–45	10–15	O. K.	O. K.	O. K.
2	3.15	93.8	76.6	5–55	9–45	O. K.	O. K.	O. K.
3	3.16	94.0	77.0	5–50	9–40	O. K.	O. K.	O. K.
4	3.16	93.6	77.4	5–55	9–35	O. K.	O. K.	O. K.
5	3.15	94.4	78.8	5–50	9–00	O. K.	O. K.	O. K.

Chemical Analysis

	Per cent
SiO_2	22.94
Fe_2O_3	4.20
Al_2O_3	4.90
CaO	62.08
MgO	1.27
SO_3	1.64
Loss	1.57
Insoluble residue	0.29

Tensile Strength (pounds per square inch)

[Average of three briquettes]

Sample	7-day mortar	7-day neat	28-day mortar	28-day neat
1	205	543	290	725
2	200	562	279	711
3	224	517	325	718
4	220	533	308	722
5	257	584	321	647

SILICA CEMENT

Specific gravity	Fineness		Time of setting		Soundness
	100-mesh	200-mesh	Initial	Final	
	Per cent	Per cent			
2.89	99.4	90.4	2–40	6–45	O. K.

Chemical Analysis

	Per cent
Soluble in HCl:	
SiO_2	13.00
Fe_2O_3	3.46
Al_2O_3	1.40
CaO	37.78
MgO	1.65
SO_3	0.87
Insoluble in HCl:	
SiO_2	31.52
Al_2O_3	6.54
MgO	0.59
Ignition loss	2.41

Possible Composition

Cement	61.3
Clay and silicious material	38.7

Tensile Strength (pounds per square inch)

[Average of three briquettes]

7-day mortar	7-day neat	28-day mortar	28-day neat
180	457	295	537

TABLE 2

Results of Tests of Sand Used in the Manufacture of Cement Drain Tile

[Specific gravity of sand=2.655]

	1 : 3 mortar briquettes	
	7-day	28-day
Washed sand	282	388
Sand as received	237	348
Sieved to pass No. 20; held on No. 30	191	283
Standard Ottawa sand	205	290

Granular Analysis of Sand

[Uniformity coefficient=3.30; per cent of silt=3.9]

Sand passing sieve No.—	Per cent
200	0.89
100	1.56
80	5.31
50	18.04
40	27.81
30	46.35
20	67.26
10	84.61
Retained on No. 10	15.38

TESTS OF MATERIALS USED IN MANUFACTURING REPLACEMENT TILE, 1914

TABLE 3

Results of Tests of Universal Portland Cement

Sample	Specific gravity	Fineness		Time of setting		Soundness		
		100-mesh	200-mesh	Initial	Final	A	W	S
		Per cent	Per cent					
1	3.09	97.2	78.9	1–20	5–15	O. K.	O. K.	O. K.

Chemical Analysis

	Per cent
SiO_2	19.84
Fe_2O_3	1.30
Al_2O_3	7.30
CaO	62.90
MgO	2.30
SO_3	1.42
Loss	2.83
Insoluble	.32

Tensile Strength

[Average of three briquettes]

7-day mortar	7-day neat	28-day mortar	28-day neat
214	527	281	664

TABLE 4

Results of Tests of Sand

[Average of three briquettes (pounds per square inch)]

	7 days	28 days
Tensile strength:		
Proportion 1–3 by weight	310	434
Compressive strength:		
Proportion 1–1½, two-inch cubes	3,545	5,863
Proportion 1–2, two-inch cubes	2,732	5,440
Proportion 1–2 (2 parts sand, 3 parts gravel), two-inch cubes	3,725	5,675

Granular Analyses

Sand passing sieve No.—	Per cent
100	1.99
50	14.39
40	21.21
30	33.31
20	48.01
14	55.78
10	66.73
8	76.63
Retained on No. 8	23.37

Gravel: All material passed the one-half-inch screen and was retained on the No. 8 sieve.

Sand was brought to the proportioning hopper, as stated above, except that it was first dropped into a large box placed on a platform scale on the upper mixing platform. All proportions were determined by weight, every batch of sand used being weighed and then dropped in the hopper above the batch mixer, where the cement was added. The material was then dropped into the batch mixer, which revolved continuously, the slide of the hopper again closed, and another batch of the material prepared. Usually one batch would be passing through the pug mill, a second being mixed in the batch mixer, and a third being prepared in the proportioning hopper so that the pug mill could be operated continually to its full capacity.

Usually one man can prepare the batches and keep the pug-mill hopper filled, but on account of the extra labor caused by the weighing of the sand two men were used while the "machine" tile were being made. Two men were also required to regulate the water supply and shovel the mixed material into the elevator boot of the Schenck machine. One man is required to operate the machine, two men are used in stripping jackets from the tile (which were placed on the car decks only a step or two away from the machine), one man is required in the sand pit, and another to push out loaded cars and bring back the empty cars, so that a total of nine men were required to operate the machine at its highest efficiency.

The quantity of water required for various batches of each series was measured by passing the water supply through a barrel whose contents were known for each inch in depth. The amount was then determined by measurement.

Due to the variation in the amount of moisture in the sand and to the use of a continuous mixer in which the water was added, it was impossible to add a predetermined or fixed quantity of water to every batch of dry material. In every case an attempt was made to make the mixture as wet as possible and still allow the immediate removal of the jacket. Too small or too great an amount of water in case of the lean mixtures will cause the tile to crumble or crack in removing the jacket or collapse during the shifting of the car. A rich mixture containing a small excess of

water will usually hang together, due to the "stickiness" of the cement, but it is likely to be distorted unless the jacket is stripped with unusual care. Too little or too much water will usually cause immediate trouble at the machine, greatly cutting down the output. The proper amount is indicated very plainly by the web like markings of neat cement on the outer surface of the tile.

The cars in use (Fig. 8) hold ninety-seven 8-inch tile, but usually the number of good tile was less, due to the sorting out of the culls, which were caused either by the failure of the machine to work properly or by carelessness on the part of the strippers in removing the jackets. This loss can be avoided and the green material remolded if the damaged tile are removed at once.

After placing in the curing room the tile were sprinkled twice, if to be steam cured—once in the evening of the day made and again during the following morning, steam having been turned on during the night. The steam-cured tile were exposed to steam for a total period of 96 hours, 16 hours per day, after which they were piled in the storage yard. The water-cured tile were sprinkled twice daily for a period of 12 days and then removed and piled in the storage yard.

The temperature of the moist air in the curing rooms varied from 110° to 120° F. during the period in which the steam was on.

The water-cured tile were allowed to harden under much more favorable conditions than are usually understood by the term "water curing." Too often "water cured" means that tile are stored in an open shed, or, at best, in a large room containing many doors and windows, and sprinkled one or more times a day. In the case of these experimental water-cured tile the cars were run into the long, narrow curing rooms which are continually damp, with wet floors, and perfectly protected from the sun and air currents. The amount of evaporation under these conditions is small compared to that in a large room or shed.

4. HANDMADE TILE

The handmade tile were made of two types, the semiwet series and the wet series. These tile have an inside diameter of 8 inches, with smooth walls 1½ inches thick and 12¼ inches long, made in sheet-metal molds provided especially for this work.

FIG. 8.—*Machine-molded cement tile, showing method of handling drain tile in a modern tile factory with 3-decked cars. The tile shown are of series 10, which have just been drawn from the steam curing chamber*

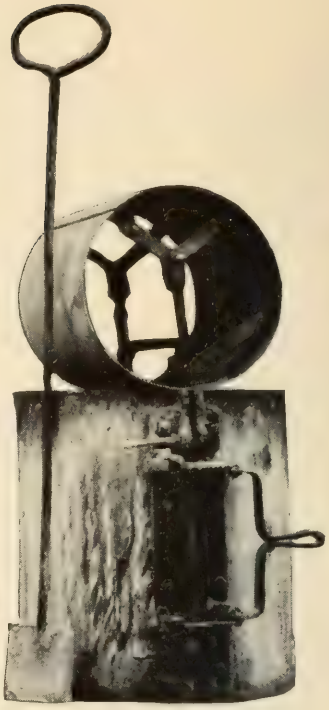

FIG. 9.—*Mold for 8-inch handmade cement tile. Sheet-metal mold consisting of outer jacket and collapsible inner core. Tamping iron used in molding tile is also shown*

FIG. 10.—*Handmade cement tile stored in yard at factory after completion of curing period. The tile in foreground are a complete set of series 1 ready for shipment*

(See Fig. 9.) The great difficulty in the use of such molds is in keeping the core centered so that the walls of the resulting tile will be of uniform thickness. Several methods were tried to secure the proper results, and the one found simplest and most satisfactory consisted of a wooden base with two concentric circles of small headless nails projecting up about three-eighth inch above the boards. These nails were placed on the inner and outer circumference of two circles having diameters of 8 and 11 inches, respectively. This arrangement provided for the centering of the lower end, but it required careful use of the tamping iron to obtain a uniform wall thickness at the top. Molds made of heavier metal would be more satisfactory in this respect, but the cost would have been excessive for this experimental series.

The process of proportioning and mixing of the materials up to the addition of the mixing water was in every way similar to that of the machine-made tile.

Series 1, 3, 4, 5, and 6 were of the plastic consistency, containing as much water as would allow the immediate removal of core and jacket. However, it was found that the material for these handmade tile had to be slightly drier than that which could be used on the machine, probably due to less pressure being exerted in hand tamping, making the tile less dense.

The semiwet handmade tile (Fig. 10) were molded on the concrete floor of one of the large curing rooms and were sprinkled in the evening of the day molded. The following morning they were again sprinkled and then placed on cars and shifted into the low-roofed curing rooms, where the steam or water treatment was continued for the proper length of time. In the manufacture of series 6, 10 per cent of ferrous sulphate, by weight, was added to a known weight of water in the measuring barrel, and this solution, kept well stirred, was used in mixing.

The tile of series 14 and 15 were made of a much wetter consistency than those of the other series. These tile contained sufficient water so that they could be easily poured into the mold from a small bucket. The tamping iron was used along the walls of the mold to aid in removing air bubbles from the surfaces. The tile of series 2 were of an intermediate consistency, and required considerable tamping in small layers in order to prevent the

formation of "rings" or roughened surfaces. The tile of these series were piled in one of the long curing chambers and sprinkled twice daily for at least 10 days.

5. CONSISTENCY OF MIXTURES USED

The following consistencies were used in the manufacture of the tile:

PLASTIC.—As much water was added to the dry-mortar mixture as would permit the immediate removal of the jacket from the tile. This condition is indicated by the weblike marks of neat cement and water on the outer surface of the wall. This consistency was used for making the tile of series 1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 16.

QUAKING.—Moisture could easily be brought to the surface by tamping. The material would settle about three-eighths inch in the mold during the first two hours after molding. This consistency was used for making the tile of series 2.

FLUID.—This material was of such a consistency that it could be easily poured into the mold. It would settle one-half to three-fourths inch in the molds during the first four hours after molding. This consistency was used for making the tile of series 14 and 15.

6. DETAILED DESCRIPTION OF EACH TYPE OF TILE

Following is a description of the tile of each of the various series, together with any notes on manufacture peculiar to each:

SERIES 1.—Proportions, by weight, one part Portland cement to two and one-half parts sand, plastic consistency, hand tamped, and cured by sprinkling. An average of 7.7 tile was obtained from each bag of cement.

SERIES 2.—Proportions, by weight, one part Portland cement to two and one-half parts sand, quaking consistency, hand tamped, cured by sprinkling with water. An average of 7.2 tile was obtained from each bag of cement.

SERIES 3.—Proportions, by weight, one part Portland cement to two parts sand, plastic consistency, hand tamped, stored in air for first 24 hours, then a total of 102 hours in steam. An average of 7.6 tile was obtained from each bag of cement.

SERIES 4.—Proportions same as series 3. Cured 24 hours in air, then dipped in neat cement grout, loaded on cars and exposed to steam for a period of 102 hours. An average of 6.9 tile was obtained from each bag of cement allowing for cement required for grouting.

SERIES 5.—Proportions and method of curing same as series 3. Tile then stored in yard and dipped in boiling tar when six weeks old. An average of 7.2 tile was obtained from each bag of cement.

SERIES 6.—Proportions and method of curing same as series 3, except that 10 per cent of ferrous sulphate, by weight, was added to mixing water. An average of 7 tile was obtained per bag of cement.

SERIES 7.—Proportions, by weight, one part Portland cement to three parts sand, plastic consistency, machine-made, steam cured. These tile were loaded on cars and placed in the curing chambers immediately after making. Steam was turned on within a few hours and continued for a total period of 96 hours. An average of 14 tile was obtained per bag of cement.

SERIES 8.—Proportions, by weight, one part Portland cement to four parts sand, plastic consistency, machine-made, cured in steam for a total period of 96 hours. An average of 18.8 tile was obtained per bag of cement.

SERIES 9.—Proportions, by weight, one part Portland cement to one and one-half parts sand, plastic consistency, machine-made, cured by sprinkling with water for a period of 12 days. An average of 8.7 tile was obtained per bag of cement.

SERIES 10.—Proportions, by weight, one part Portland cement to one and one-half parts sand, plastic consistency, machine-made, cured in steam for a period of 96 hours. This series differs from series 9 only in the method of curing. An average of 8.7 tile was obtained per bag of cement.

SERIES 11.—Proportions, by weight, one part Portland cement to three parts sand, plastic consistency, machine-made, cured by sprinkling for a period of 12 days. This series differs from series 7 only in the method of curing. An average of 13.7 tile was obtained per bag of cement.

SERIES 12.—Proportions, by weight, one part Portland cement to four parts sand, plastic consistency, machine-made, cured by sprinkling for a period of 12 days. This series differs from series 8 only in the method of curing. An average of 18.4 tile was obtained per bag of cement.

SERIES 13.—Proportions, by weight, one part Portland cement to two and one-half parts sand, plastic consistency, machine-made, cured in steam for a total period of 96 hours. An average of 12 tile was obtained per bag of cement.

SERIES 14.—Proportions, by weight, one part Portland cement to three parts sand, fluid consistency, hand tamped, cured by sprinkling for a period of at least 12 days. Greater part of settling of material in molds took place during the first hour, after which the molds were refilled with some of the same material tamped and troweled. An average of 8 tile was obtained per bag of cement.

SERIES 15.—Proportions, by weight, one part sand-cement to three parts sand, fluid consistency, hand tamped, cured by sprinkling with water for a period of at least 10 days. Molds refilled with same material, tamped and troweled, after settling had taken place. These tile required very careful handling when the molds were removed on the day after molding to avoid breakage. An average of 7.4 tile was obtained per bag of cement.

SERIES 16.—Proportions, by weight, one part Northwestern States Portland cement to four parts sand, plastic consistency, machine-made, cured in steam. This series, which was taken from the stock pile of the Armstrong Cement Works, represents the regular commercial output of this factory. No especial care was used in selection, except to throw aside tile which were cracked or had jammed ends. The exact age of this series is uncertain but the tile are probably at least six months older than those of the preceding series.

The machine-made tile varied in weight from 23 to 25.25 pounds, averaging 24 pounds; the semiwet hand-tamped tile varied in weight from 42.25 to 45 pounds, averaging about 43.2 pounds; tile in series 15, sand-cement, averaged about 41.5 pounds.

The difference in appearance of the surfaces of the different series is shown in Figs. 11 to 14. The appearance varies with the

FIG. 11.—*Handmade tile of series 2, made of a quaking consistency mortar, and machine-made tile of series 7, made of plastic consistency mortar, showing the texture of the surface and relative size of the two types*

FIG. 12.—*Appearance of machine-made tile of rich and lean mixtures. Tile marked 10 is composed of one part cement to one and one-half parts sand; tile 7, one part cement to three parts sand; and tile 12 and 16 are one part cement to four parts of sand, all made by the same process excepting 12, which was cured by sprinkling instead of exposing in steam*

FIG. 13.—*Appearance of handmade tile of different consistencies. Tile marked 1 was made of plastic consistency; 2 of quaking consistency, and 14 of fluid consistency. Tile 1 and 2 are composed of one part cement to two and one-half parts of sand; tile 14 of one part cement to three parts sand*

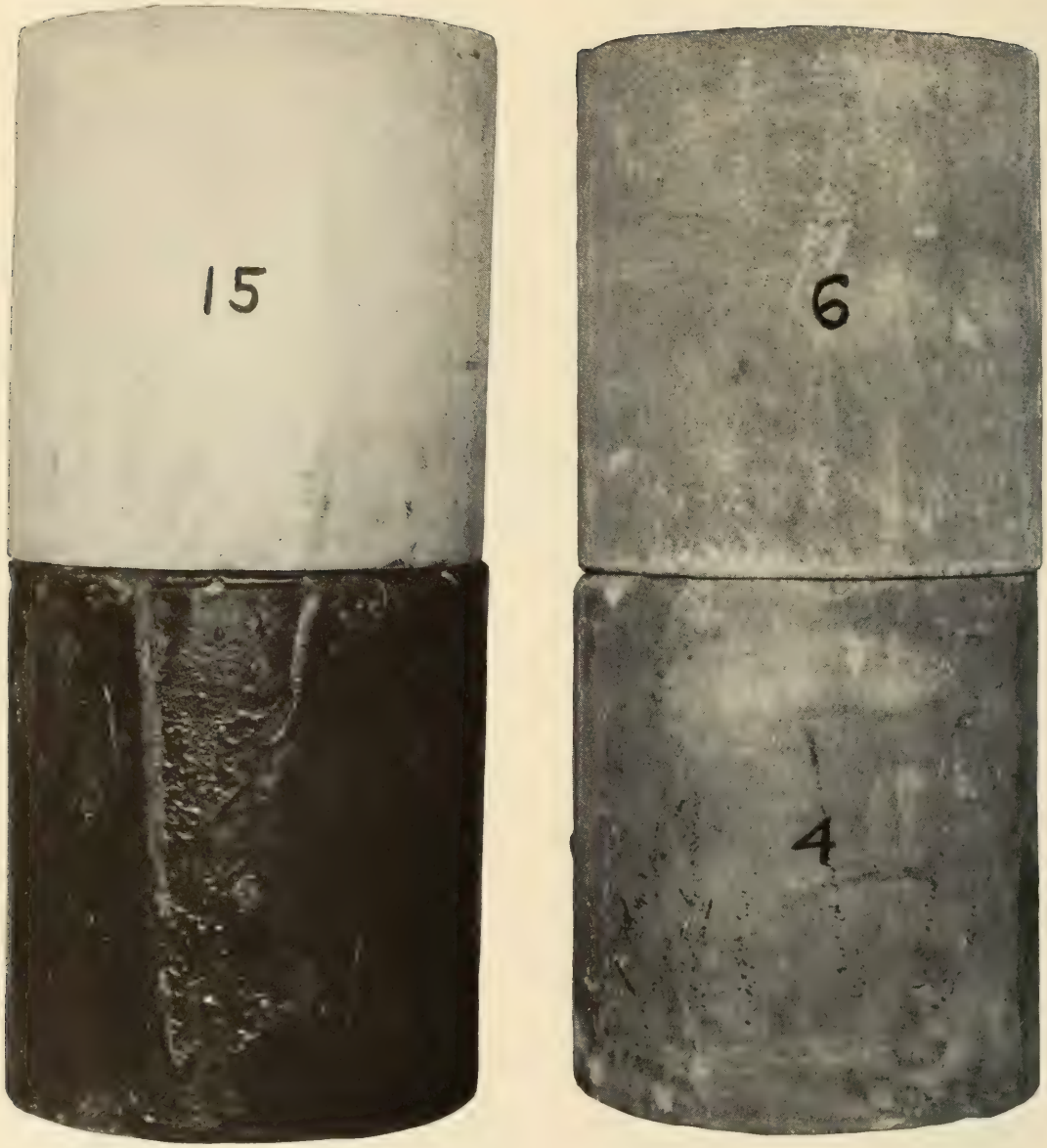

FIG. 14.—*Appearance of special and treated tile. Tile of series 4, 5, and 6 were all made by the same process. No. 4 was dipped in cement grout, 5 in hot tar, and 6 was treated by adding ferrous sulphate to the water used in mixing. Tile of series 15 were made of one part sand-cement to three parts of sand mixed to a fluid consistency*

richness of the mixture as well as the method of molding. Of the machine-made series, 9 and 10, the richest, are lightest in color with more of a glazed appearance while the leaner mixtures are darker in color and have more of a sandy, roughened appearance. In the handmade series, No. 15 is nearly white with a "chalky" appearance, due to the use of sand-cement. In series 2, 14, and 15 the handmade tile of quaking and fluid consistency have rather smooth surfaces with numerous small and shallow indentations due to air pockets on the walls of the molds. The plastic mixtures of the handmade tile series 1, 3, and 6 have rough surfaces as a rule and in a few cases irregular and insufficient tamping was indicated by the appearance of circumferential rings of porous appearing concrete.

Throughout this work no departure from the regular processes in use at this plant were made except that the proportions were varied and all the materials were weighed to insure uniformity. No specially chosen aggregates were used, the sand being that used in the factory for the manufacture of all kinds of cement products and the cement being purchased under bids with the requirement that it was to pass the United States Government specification for Portland cement. Although some of the mixtures contain more cement than those in ordinary commercial use, and it is not practicable to make a handmade tile which can compete in price with the usual machine-made tile, any well equipped and managed factory using good materials should be able to turn out a product which is as good in every respect as has been provided for this investigation.

7. REPLACEMENT TILE

The tile supplied to replace those tested during the year 1914 were supplied by the Universal Portland Cement Co., and were designated by the series numbers 17 and 18. These tile were 12 inches in length, of 8 inches inside diameter, with a wall thickness of 0.8 inch.

All concrete was machine mixed, sufficient water being added that the mixture would just hold its shape when piled with a shovel and would not splash out of the molds when agitated. The

sheet-metal molds were filled with an excess of material in a funnel attached to the top of the form. The mold was then placed upon the jigging-machine platform and the machine operated for a period of 30 seconds. The drop of this platform was $\frac{13}{32}$ inch while the platform made 120 complete trips through this space per minute.

Two sizes of aggregate were used, a sand of good quality passing the one-fourth inch screen and a gravel passing a one-half inch round opening and retained on a No. 8 sieve. The sample of cement used in the manufacture of these series was lost in transit and the results shown in Table 3 were obtained on a sample of the same brand of cement which was submitted six months later. The proportions used were as follows:

SERIES 17.—One sack of cement to 1½ cubic feet of sand.

SERIES 18.—One sack of cement to 2 cubic feet of a mixture of fine and coarse aggregates, which were mixed in the proportion of two parts sand to three parts one-fourth inch to one-half inch gravel.

The tile were removed from the molds on the following day and then piled in one corner of the laboratory and covered with sand which was kept constantly wet.

The surface of these tile had much the same appearance of that of the tile of series 2, 14, and 15, since they were made of a quaking consistency.

After these tile had cured for a period of at least one month they were crated in wooden crates holding six tile each and shipped to the various projects and later installed in the place of those removed for test.

IV. INSTALLATION OF DRAIN TILE

1. SHIPMENT

Shipments of the tile from the factory at Armstrong, Iowa, were made early in October, 1913. A carload (about 780 tile) was shipped to each project, each shipment consisting of 50 tile of each series, with the exception of series 5 and 15, of which 45 and 36, respectively, were sent. The tile were piled with their walls parallel to the car sides beginning at either end, and tiered

three and four high, depending upon the length of the car. This arrangement was continued up to within 3 feet of the doorway where the number of layers was reduced to two and then one. The doorway space was occupied by several rows one tile high, placed so as to block the lower layer in the two ends. To reduce the breakage a thin layer of straw was spread over the floor and between the layers. The cars arrived at their destination showing little evidence of the tile having been thrown out of place while in transit, although no framing whatever was used to keep them in position. Breakage was due almost entirely to wedging of tile in the lower layers. This wedging action was probably aided by the "giving" of the car sides while in motion. In some cases no record of breakage was kept at the time of unloading, so that the following figures include the loss in unloading and hauling of the tile at destination.

The length of wagon haul and the total breakage is recorded in the following table:

Location	Wagon haul	Loss	Location	Wagon haul	Loss
Garland.....miles..	3½	3	Grand Junction.....miles..	2	9
Fort Shaw.....do..	1	3	Montrose.....do..	12	22
Huntington.....do..	24	18	Columbia.....do..	1½	22
Sunnyside.....do..	1	8	Crookston.....yards..	800	6
Yuma.....do..	2	18	Ames.....feet..	400	3
Roswell.....do..	5	4			

A total of 116 tile were broken out of over 8500 shipped, an average railway haul of about 1300 miles, and a wagon haul of over 4.5 miles. The average loss by breakage is 1.3 per cent.

2. COMPOSITION OF ALKALI AND SOIL AT DRAIN SITES

The character of alkali found at the site of the drains is given in Table 5. The alkali samples were obtained by scraping the salts from the surface of the ground at all points excepting at Crookston, Minn., and Columbia, Mo., where soil samples only were taken. The composition and concentration of alkali in the soil at the level of the drain is given in Table 6. Analyses of the waters flowing in the various drains are given in Table 7.

The analyses of the alkalies, soils, and waters are given in percentages of the soluble or dissolved material present. Figs. 15, 16, and 17 show graphically the results calculated on the basis of percentage reacting values as discussed by Stabler in Water Supply Paper 274, and Palmer in Bulletin 479 of the United States Geological Survey.

The reacting value is the chemical reacting power of the radicle in terms of the hydrogen equivalent and may be calculated in a number of ways. The reacting values included in this paper were obtained by multiplying the weight of the radicle in milligrams by the reaction coefficient. The reaction coefficient was obtained by dividing the valency of the radicle by its combining weight. Expressed as an equation

$$\text{Reacting value} = \frac{\text{Weight of ion or radicle in milligrams} \times \text{valency}}{\text{combining weight}}$$

For example:

Reacting value

$$\text{Na} = \frac{\text{Weight in mg} \times 1}{23.1} = \frac{\text{Weight in mg}}{23.1} = .0433 \text{ weight in mg.}$$

$$\text{SO}_4 = \frac{\text{Weight in mg} \times 2}{96} = \frac{\text{Weight in mg}}{48} = .0208 \text{ weight in mg.}$$

The percentage reacting value of each radicle was then determined.

TABLE 5

Analyses of Alkalies from Surface of Ground at Site of Drain November, 1913

[Analyses of mineral matter in per cents]

Location	Na_2O	K_2O	CaO	MgO	SO_3	Cl
Garland, Wyo.	41.54	0.56	0.76	0.60	56.36	0.60
Fort Shaw, Mont.	34.45	.26	3.22	1.75	59.20	1.07
Sunnyside, Wash. (Station No. 1)	30.20	.22	.84	9.28	50.20	9.27
Roswell, N. M. (Station No. 15+15)	13.60	2.43	21.92	7.68	33.65	20.60
Montrose, Colo.	11.27	None.	2.58	39.80	46.40	.03
Grand Junction, Colo.	35.66	None.	.91	10.22	37.40	15.82
Huntington, Utah	36.88	.74	3.30	4.10	55.00	.12
Yuma, Ariz.	26.68	.32	8.23	12.67	10.00	42.10

TABLE 6

Analyses of Soils at Level of Tile Drains November, 1913

[Analyses of mineral matter in per cents]

Location	Per cent soluble solids	Na_2O	K_2O	CaO	MgO	SO_3	Cl	CO_2	SiO_2
Garland, Wyo	0.85	11.41	Trace.	33.17	None.	54.56	0.88	.....	.....
Fort Shaw, Mont	2.82	20.40	.....	18.38	2.04	58.15	.58	0.45	.....
Sunnyside, Wash	.52	25.57	Trace.	7.42	4.34	47.52	4.62	.....	10.53
Yuma, Ariz	.14	24.40	Trace.	18.42	9.05	15.36	9.76	23.11	.....
Roswell, N. Mex	.19	35.58	.....	12.48	1.43	23.52	11.25	15.74	.....
Montrose, Colo	.91	14.12	Trace.	22.70	5.68	55.65	1.85	.....	.....
Grand Junction, Colo	.78	26.83	Trace.	13.02	4.27	40.42	15.46	.....	.....
Huntington, Utah	.99	3.41	Trace.	36.14	3.55	56.60	.30	.....	.....

TABLE 7

Analyses of Seepage Waters Flowing Through Experimental Cement Tile Drains November, 1913

[Analyses of mineral matter in per cents]

Location	Per cent soluble solids	SiO_2	R_2O_3	CaO	MgO	Na_2O	Cl	SO_3	CO_2	Sediment
Garland, Wyo	0.499	0.88	0.10	5.40	3.00	35.00	2.97	49.32	3.55	Very small amount.
Fort Shaw, Mont. (station No. 2).	.649	.50	.07	4.66	6.71	31.28	1.82	51.23	3.85	Do.
Fort Shaw, Mont. (station No. 9).	.237	.96	.21	6.15	10.72	27.68	2.15	38.30	13.83	Do.
Sunnyside, Wash	.593	.84	.10	11.83	6.39	23.58	7.06	47.12	3.07	None.
Roswell, N. Mex. (station No. 11).	.531	.32	.09	20.22	3.97	19.16	22.63	30.52	3.03	Considerable.
Roswell, N. Mex. (station No. 17+74).	.525	.55	.11	14.95	4.69	23.76	27.58	26.02	2.31	Some.
Montrose, Colo	1.005	.32	.03	6.87	19.53	11.87	.49	57.95	2.97	None.
Grand Junction, Colo. (outlet).	1.165	.24	.08	7.14	7.34	27.93	24.82	32.02	.45	Do.
Huntington, Utah	.253	.76	.15	21.58	6.69	14.26	2.10	47.40	7.05	Considerable.
Yuma, Ariz. (upper end).	.090	3.68	.78	16.71	8.13	20.82	20.82	11.47	11.59	Very smal amount.
Grand Junction, Colo. (irrigation water; from irrigation canal).	.081	2.72	.12	13.86	5.80	23.90	22.03	22.03	9.53	Do.

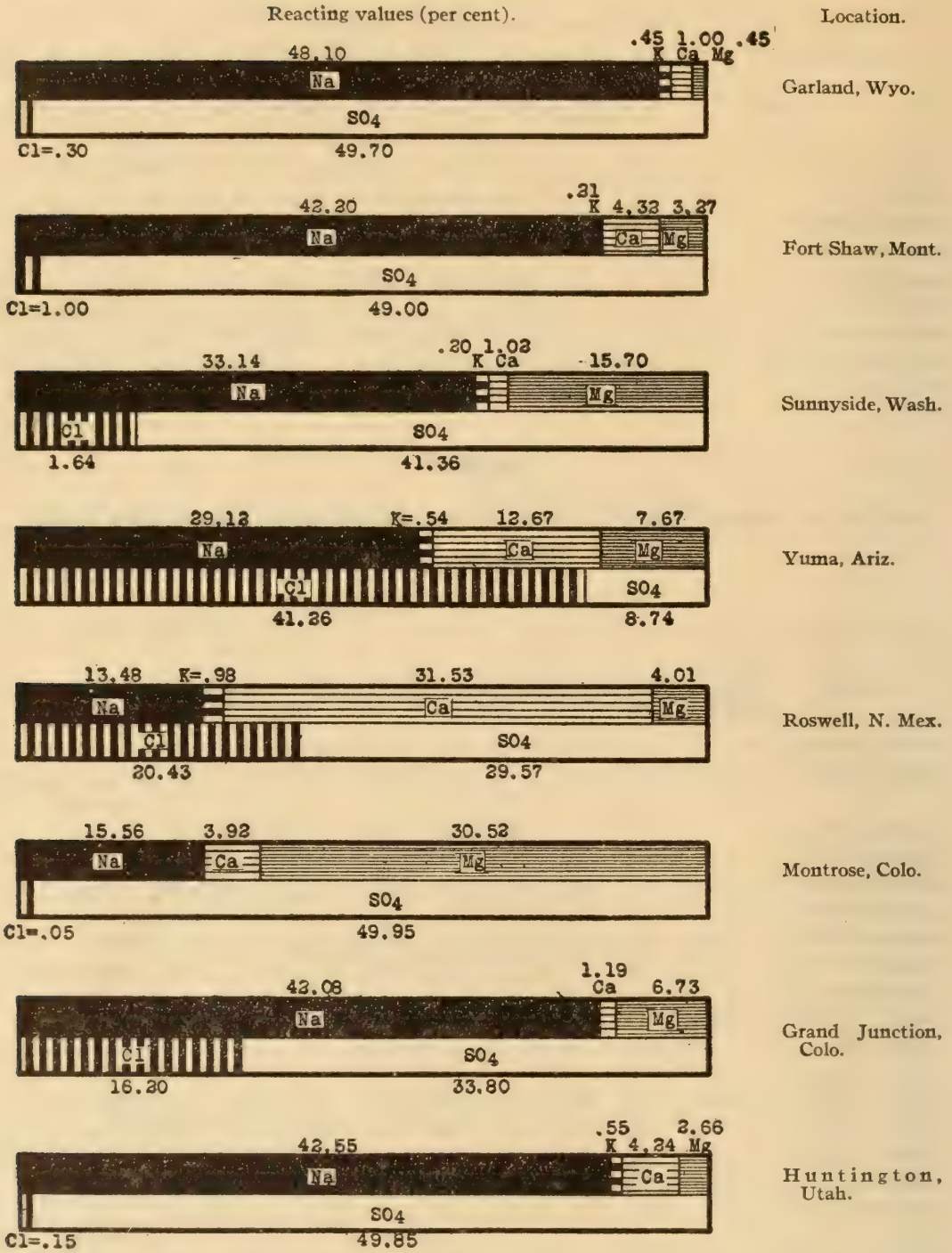

FIG. 15.—*Chemical analyses of alkali salts from surface of ground at site of experimental cement tile drains (1913). (Results given in Table 5)*

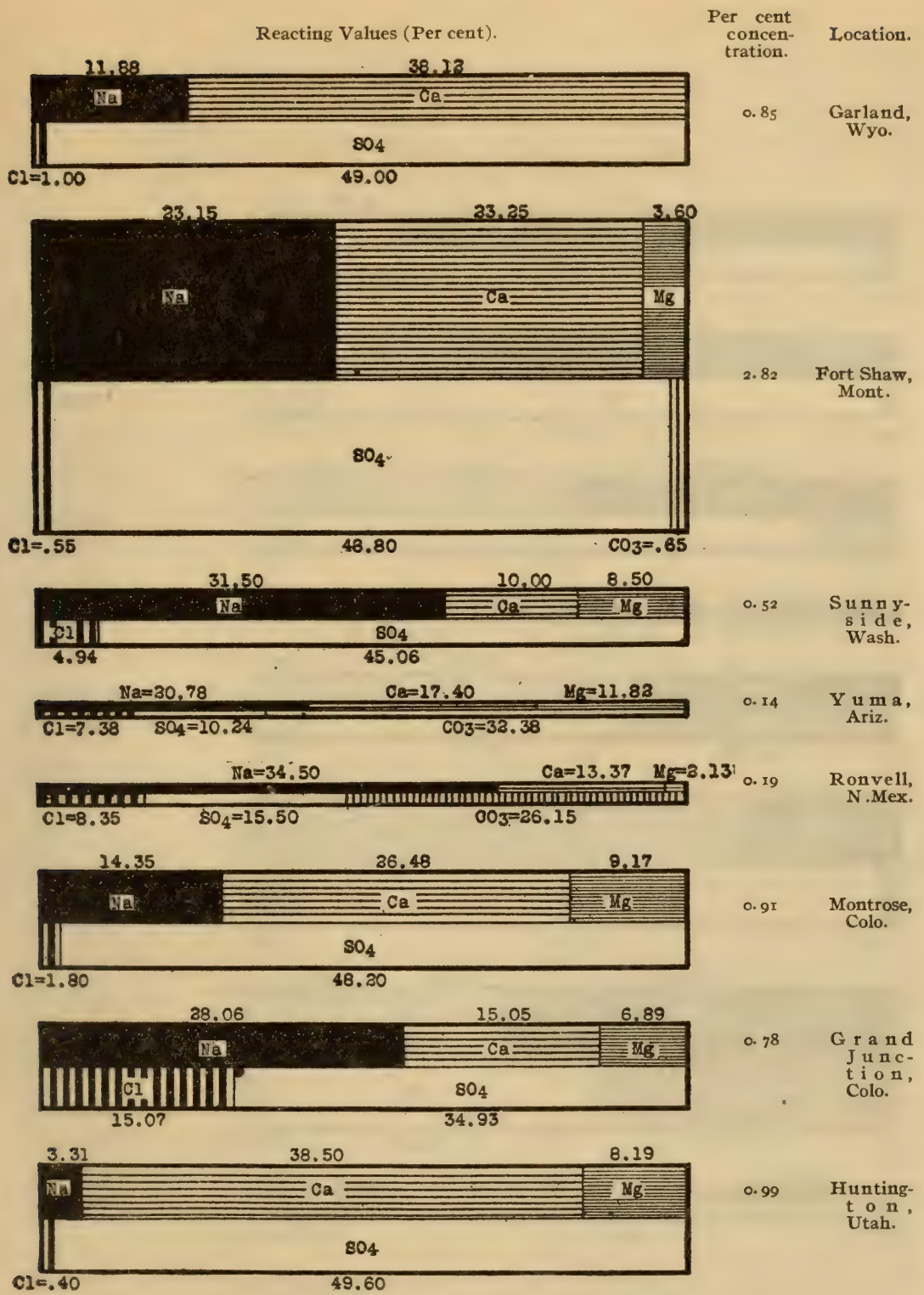

FIG. 16.—*Chemical analysis of soils at level of experimental tile drains (1913). (Results given in Table 6)*

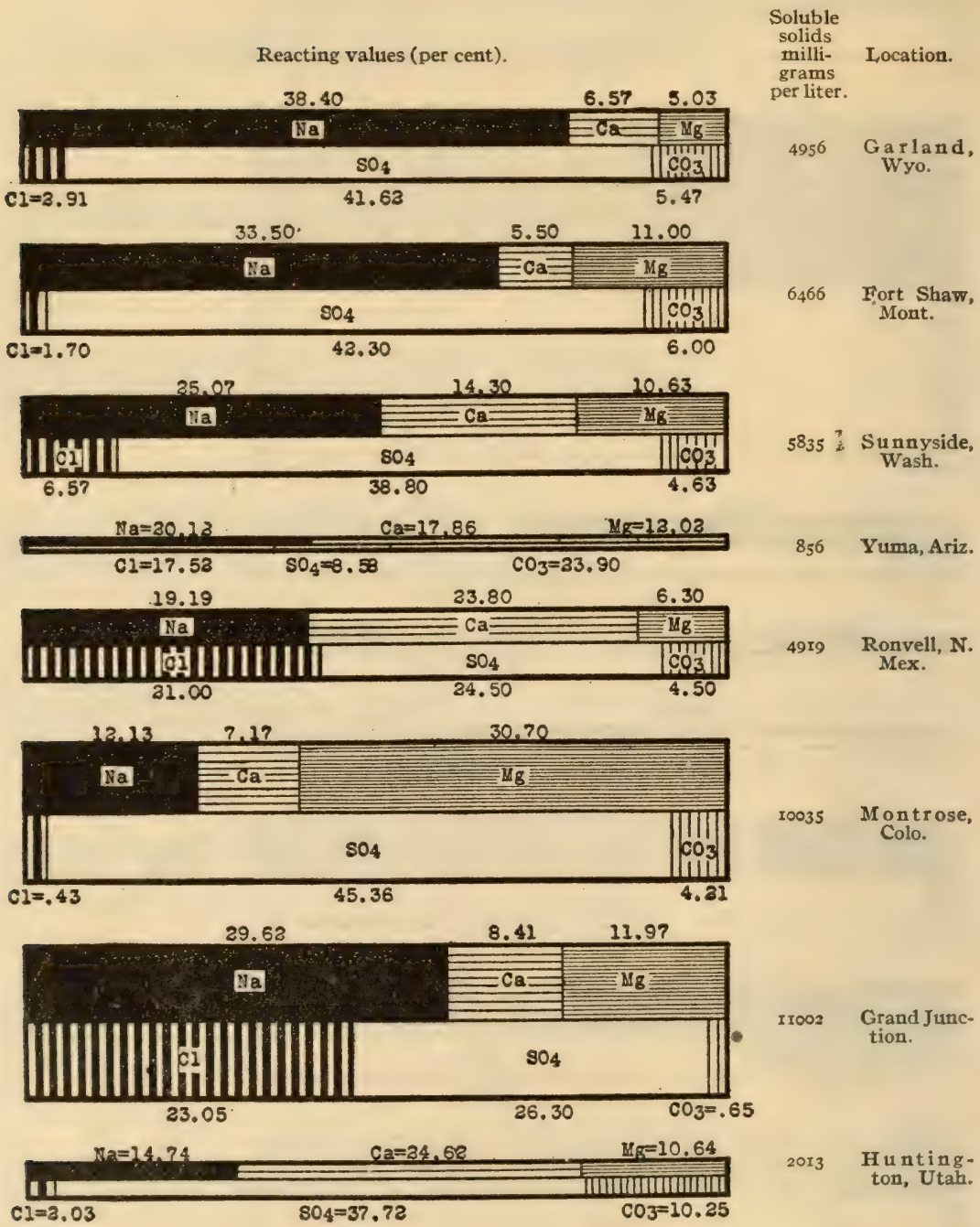

FIG. *17.—Chemical analyses of seepage waters flowing through experimental cement tile drains (1913). (Results given in Table 7)*

3. PLACING

The tile were placed in such an order that sections containing two tile of each series could be removed at yearly intervals without disturbing the remainder of the line. Ten such sections, 32 feet long, were placed at one end of the line, and then all the tile remaining of each series were placed end to end in groups, commencing with series 1. This grouping is shown in Fig. 18. At Garland, Fort Shaw, Sunnyside, Yuma, and Roswell the "A" sections were placed at the upper end of the drain and the "B" sections at the outlet end. At the other points this arrangement of sections was reversed.

(*a*) GARLAND, WYO.—The drain was placed about 3½ miles southeast of Garland in a low section where alkali stood in layers an inch or more in thickness on the ground. Several concrete turnouts located near by in unused ditches were entirely disintegrated. As shown in Fig. 19, the lower end of the drain runs through a sandy soil and the upper end through coarse gravel, the grades being 0.022 and 0.010, respectively. The outlet is in an open ditch, which has a grade of 0.002. Since the oulet end for a distance of 200 feet lies above the frost line, a back fill was made, giving a minimum covering of 4 feet.

The tile were laid in cradles made of 2 by 4 inch side pieces and 1 by 4 inch cross pieces, on which the tile rested. Manholes were placed at stations 3+50 and 4+50, at an angle point and change of grade. At the time the tile were placed the groundwater plane was at the surface of the ground for the entire distance. Photographs were taken during the placing of the tile, which are shown in Figs. 20 and 21. The total fall in the line is 11 feet. Only three tile were broken or missing at Garland, the number being unusually low considering the length of the haul.

(*b*) FORT SHAW, MONT.—At Fort Shaw a location for the tile line was found just above an alkali lake, where the tile would also be of some service in draining an upper swamp which had ruined several farm units. The surface of the ground surrounding the lake and the site of the drain was incrusted with alkali one-eighth to one-fourth inch in thickness. Wooden silt boxes were placed at the upper end at station 6+00, where an angle was made.

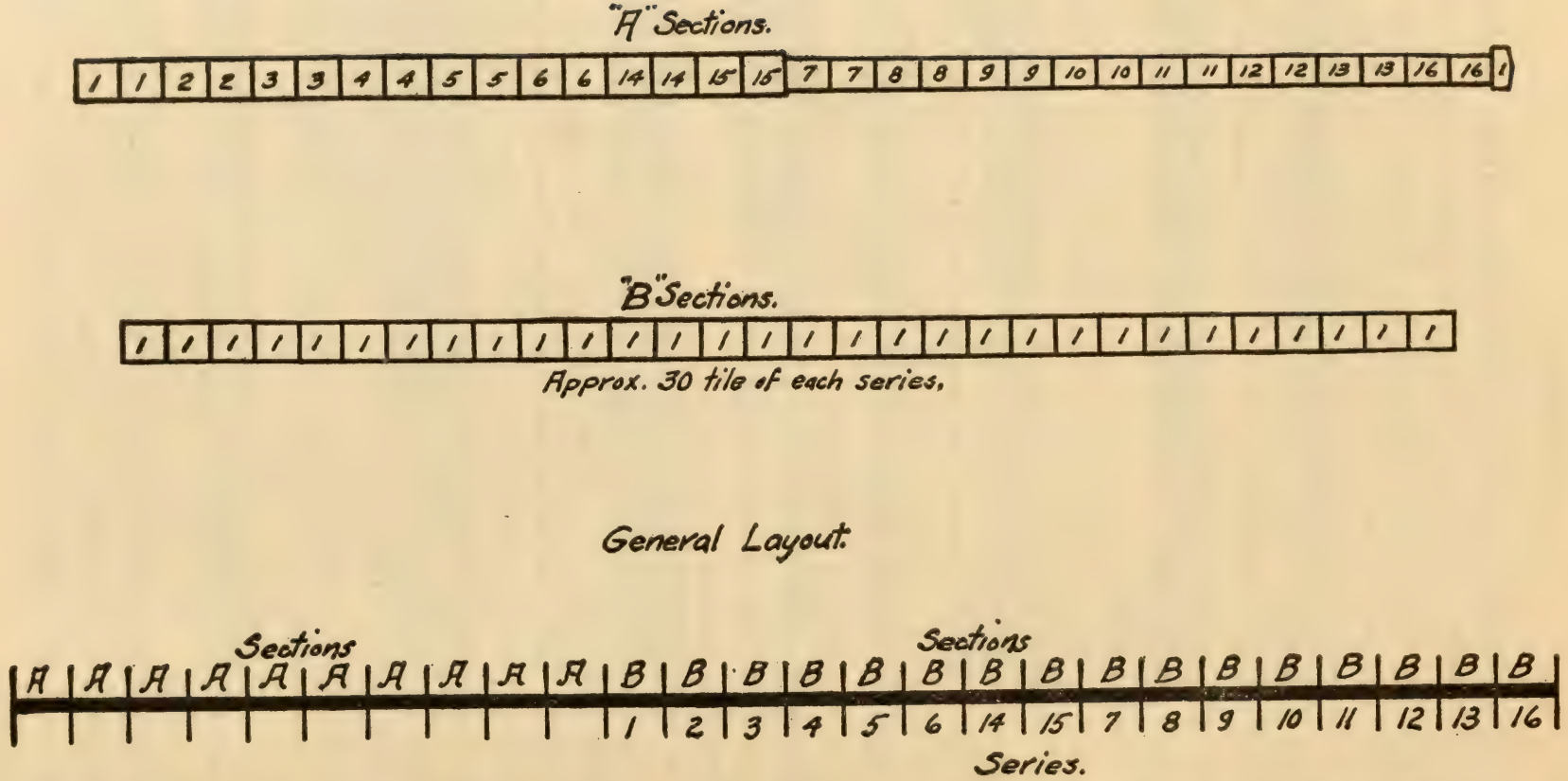
"A" Sections.
1 1 2 2 3 3 4 4 5 5 6 6 14 14 15 15 7 7 8 8 9 9 10 10 11 11 12 12 13 13 16 16 1
"B" Sections.
Approx. 30 tile of each series.
General Layout.
Sections
A A A A A A A A A A
Sections
B B B B B B B B B B B B B B B B B B B B
1 2 3 4 5 6 14 15 7 8 9 10 11 12 13 16
Series.

FIG. 18.—*Arrangement of drain tile. The "A" sections contain two tile of each series and were thus arranged for convenience in removal for testing. There are 10 "A" sections followed by "B" sections each of which is composed of all the remaining tile of one type*

As the greater portion of the drain was located above the frost line, the refill was made to a depth of 4 feet wherever the cut was less than this amount. A portion of the line passed through hard cemented gravel, which gave considerable trouble in digging. The upper 400 feet of the line was given a grade of 0.021 and the lower 200 feet a grade of 0.004, the outlet being into an open ditch which emptied into the alkali lake 200 feet below the tile line. Three tile were broken in this shipment. Figs. 22, 23, and 24 show the location of this drain.

(*c*) HUNTINGTON, UTAH.—At Huntington the tile drain was installed on private land about 1 mile south of town. Wooden box drains, without bottoms, had been placed in this ground about eight years before, and as these boxes were filled and badly off grade it was decided to replace them with cement tile.

As shown in Fig. 25 the line of the old wooden drain was not closely followed, but an offset was made and the old line paralleled. The trench varied in depth from 4½ to 6 feet, passing through a soil uniform in color and appearance, and acting much like quicksand in the bottom, due to the excess of water. The digging was very easy, requiring no picks or spades but only round-pointed long-handled shovels. The drain was laid with a fall of approximately 1 foot per 100 feet. In the portion of the trench which followed the old box drains the tile were supported on boards 1 inch by 6 inch by 12 feet on account of the soft bottom. Figs. 26 and 27 show the conditions near the site of the drain.

On account of rains preceding the installation of the experimental tile, the white surface of this and the surrounding land was not so apparent, but in spots large white patches could be seen. Land to the west and slightly higher than that on which the tile were placed was very wet and sandstone bowlders lying on the surface were badly cracked and disintegrated, apparently due to the crystallization of the alkali in their pores.

As Huntington is located about 23 miles from the railroad it was necessary to haul the tile from Price, Utah. The number of tile broken was 18, confined mostly to the handling on the railroad as only 4 tile were broken in the 24-mile haul from Price.

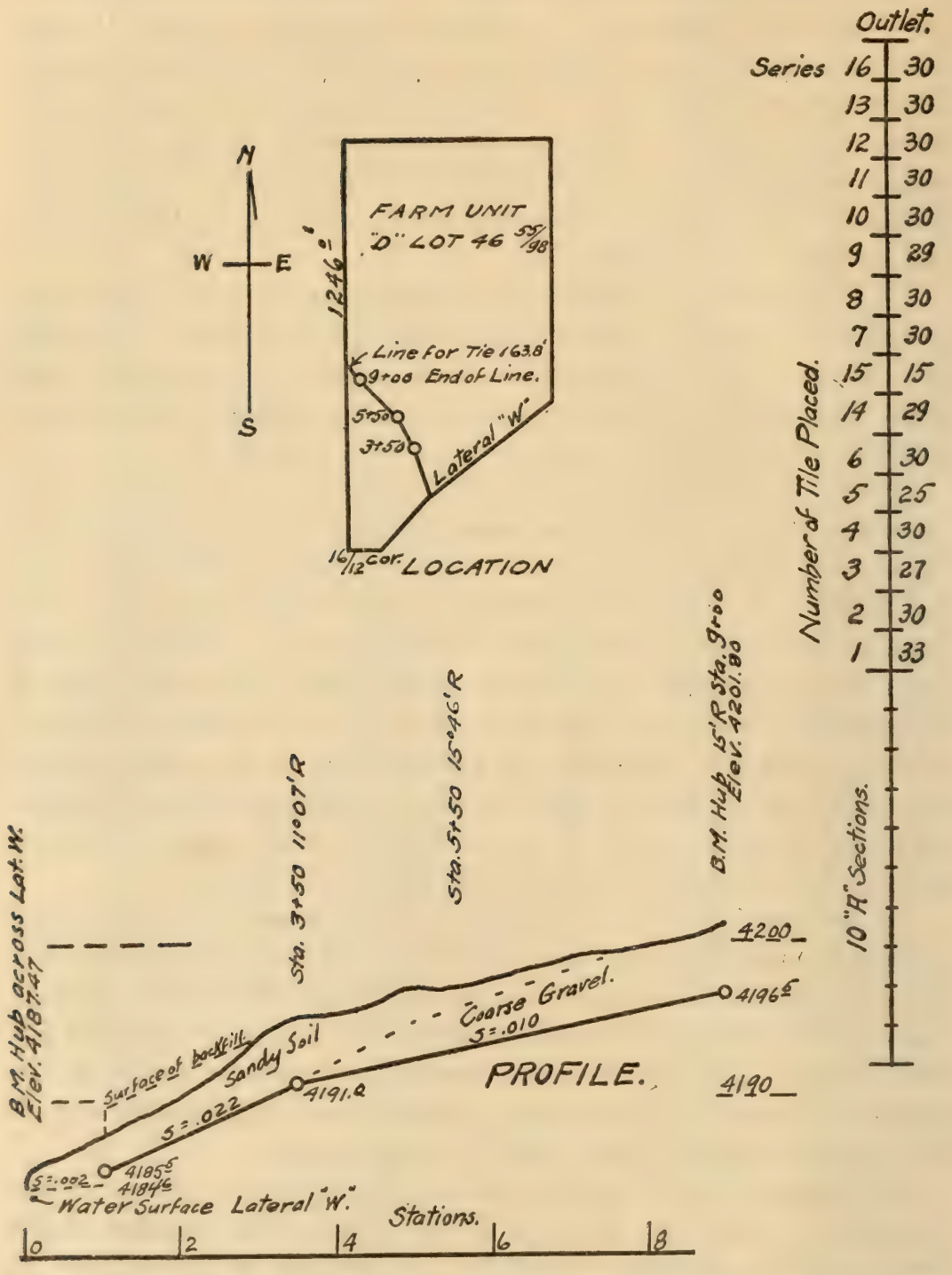

FIG. 19.—*Showing location, plan, profile, and arrangement of experimental drain tile at Garland, Wyo.*

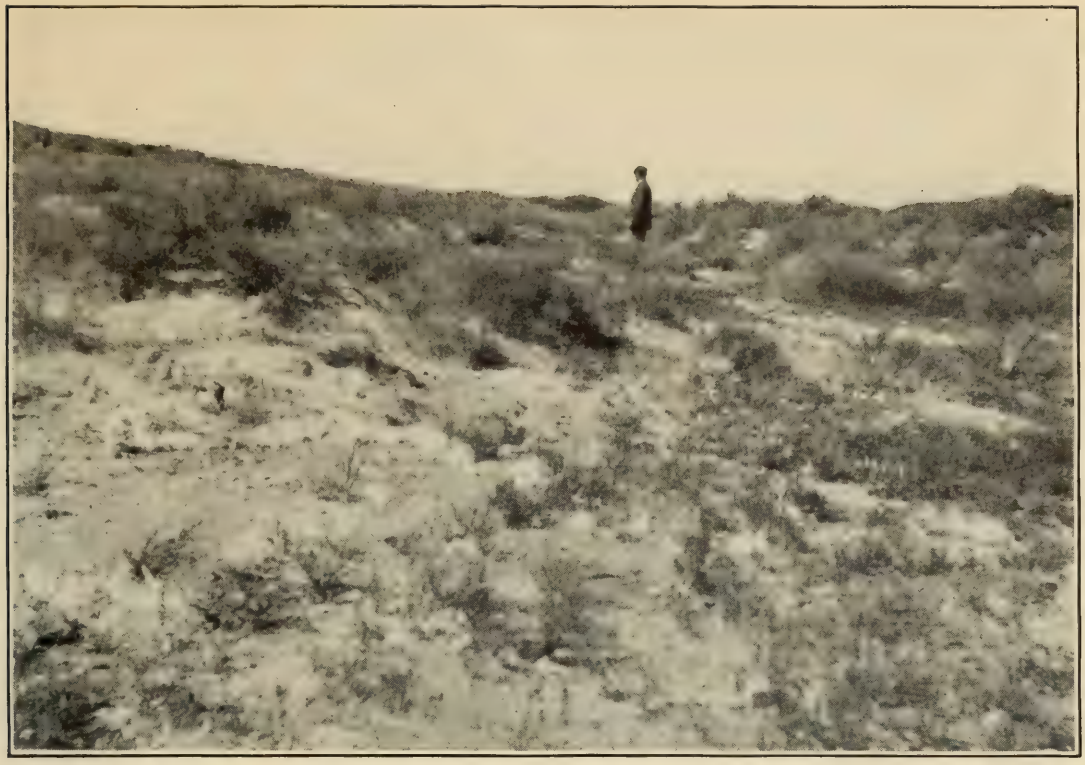

FIG. 20.—*Site of experimental drain, lower end, at Garland, Wyo., showing heavy incrustations of alkali on surface and character of the vegetation. This site is usually swampy from seepage water, and the alkali concentration may be considered as bad as any to be found in the State*

FIG. 21.—*View of opened ditch at silt basin experimental drain at Garland, Wyo., showing the gravel soil and seepage water in the trench above the grade of the drain; also the wooden cradles shown on the left upon which the tile were placed*

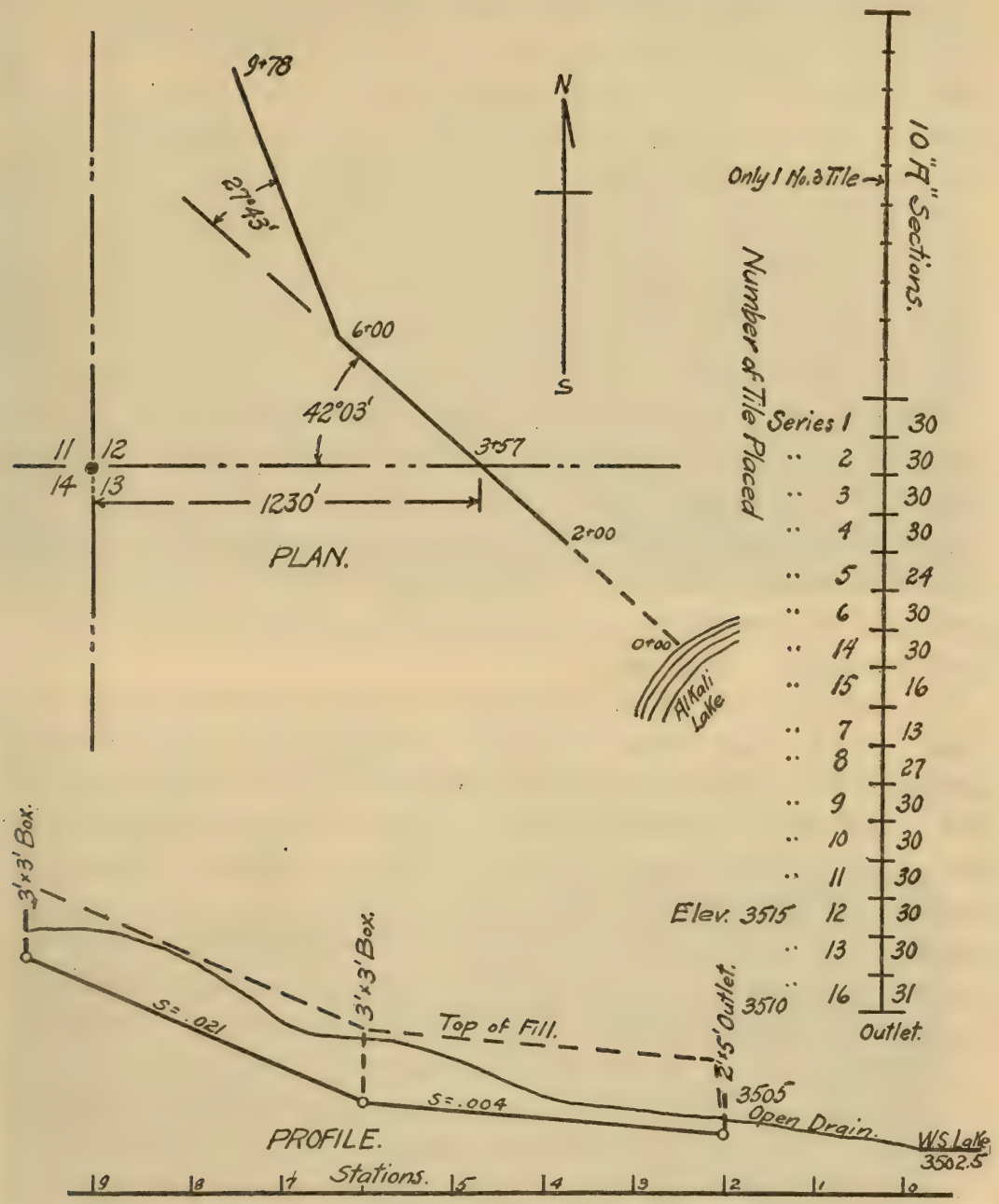

FIG. 22.—*Showing location, plan, profile, and arrangement of experimental drain tile at Fort Shaw, Mont.*

(*d*) SUNNYSIDE, WASH.—At Sunnyside the tile were installed on private land about 1 mile from town. The trench at the lower end was about 6 feet deep and 4½ feet deep at the upper end. At the lower end the soil was very sandy. The water table was low at the time the tile were placed. A uniform grade of 0.002 was used. There was a loss of eight tile in this shipment. The location of this drain is shown in Fig. 28. Figs. 29 and 30 show the conditions at this point.

(*e*) YUMA, ARIZ.—The installation at Yuma was made in the southeast corner of the experiment farm of the United States Department of Agriculture on the Yuma Indian Reservation. The drain follows the line of an old slough and is exposed to concentrated alkali water. The wagon haul to this point was about 2 miles and the total number of tile lost, including railroad breakage, was 18. Fig. 31 shows the location of this drain. Figs. 32 and 33 show the installation of the drain.

(*f*) ROSWELL, N. MEX.—The installation at Roswell was made on private land 4 miles east and 1½ miles north of Roswell on the northeast quarter of sec. 25, T. 10 S., R. 24 E., New Mexico principal meridian. (Fig. 34.)

The outlet of the line was placed in the wooden manhole of a drain which had been previously constructed and extended northeast in a straight line with a uniform rise of 0.1 foot per 100 feet. The depth averaged about 6.5 feet, with the exception that the upper 150 feet had a depth of about 5.5 feet. During the installation the ground water stood about 4 feet above grade, causing the sides of the trench to cave unless well braced. A wooden manhole was placed at the end of the tenth "A" section, and an observation well at the upper end of the line. Three tile were found broken in the car and one was broken in hauling to the drain site, so that the breakage was approximately one-half of 1 per cent. Fig. 35 shows the work in progress at Roswell.

(*g*) GRAND JUNCTION, COLO.—The tile at Grand Junction were placed on a 10-acre tract of land included in the McKinney experimental farm, one-fourth mile south of the old United States Indian school just east of the city. (See Fig. 36.) The land of which this tract is a part is being improved under the supervision

FIG. 23.—*Alkali Lake at lower end of experimental drain at Fort Shaw, Mont., showing the heavy alkali deposits surrounding the lake*

FIG. 24.—*Site of experimental drain at Fort Shaw, Mont., looking toward lower end, showing the partially excavated trench and alkaline seepage water collecting in the bottom; also alkali weed covering the site*

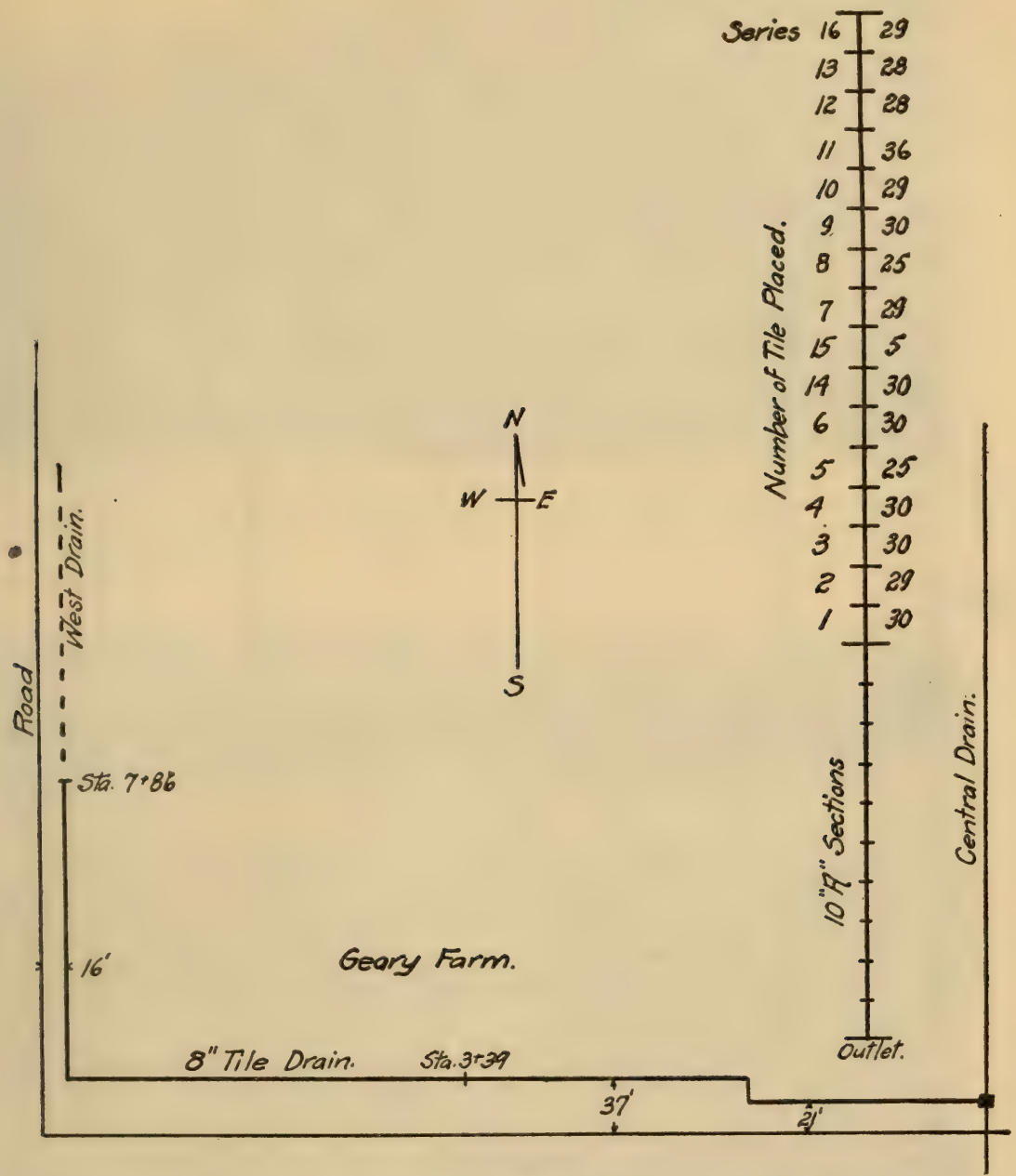

FIG. 25.—*Showing location, plan, and arrangement of experimental drain tile at Huntington, Utah*

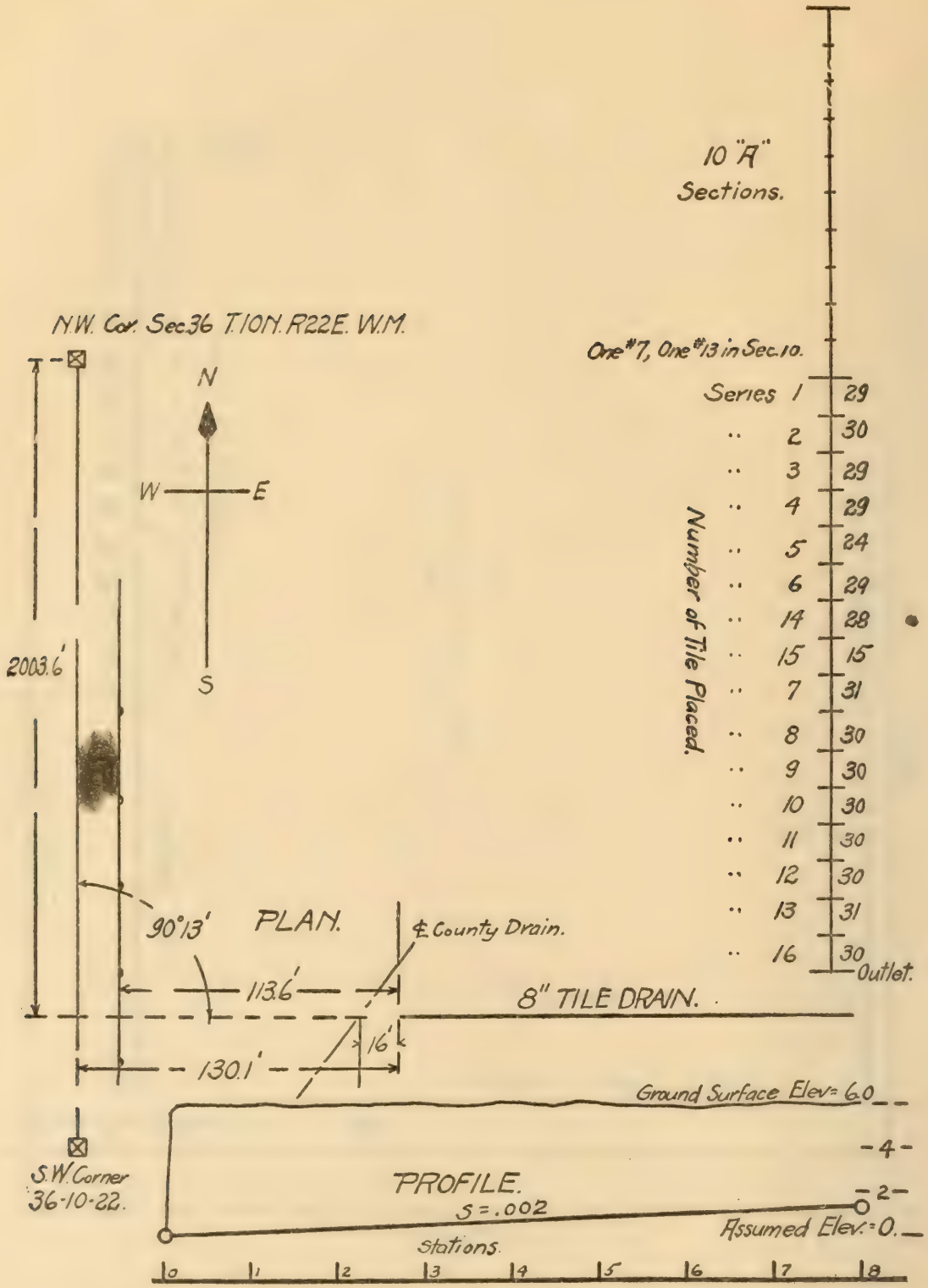

FIG. 28.—*Showing location, plan, profile, and arrangement of experimental drain tile at Sunnyside, Wash.*

FIG. 26.—*Opened ditch for experimental drain at Huntington, Utah, showing the character of the soil, lack of vegetation due to alkali salts, and the approximate depth of excavation*

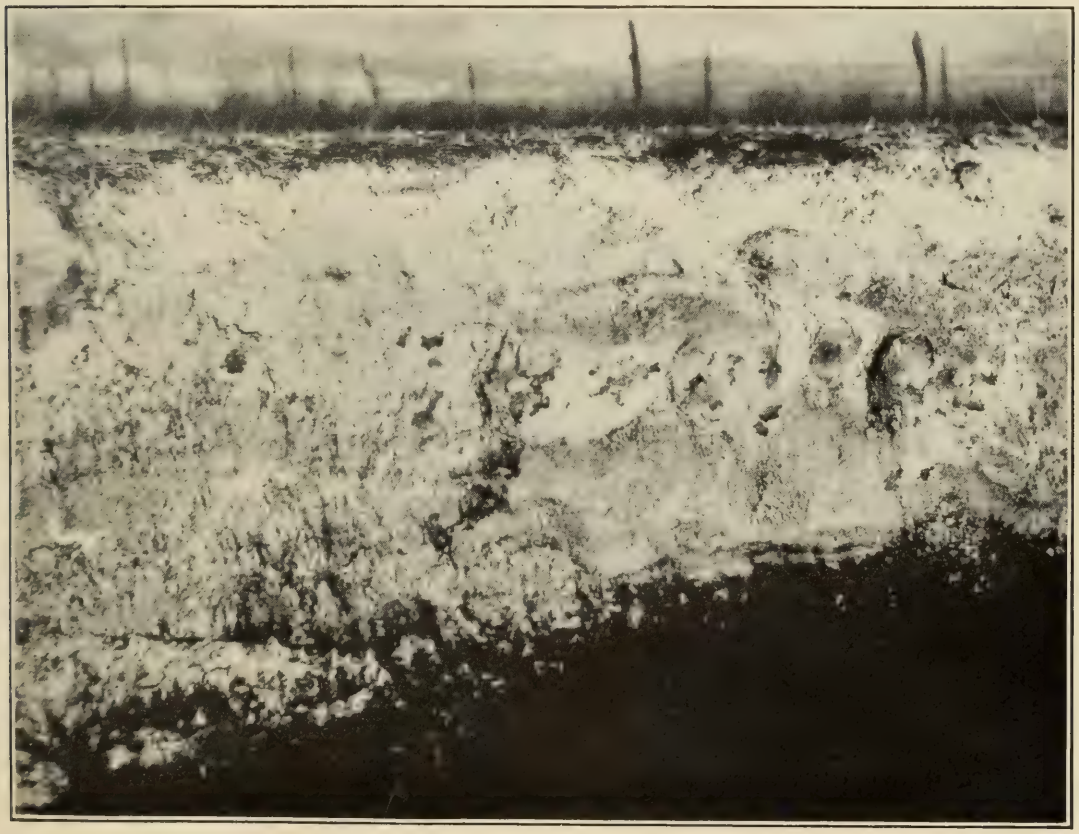

FIG. 27.—*Bank of waste ditch, showing heavy white incrustation of alkali salts at Huntington, Utah. The concentration of alkali salts in this locality is probably as great as will be found in the State*

FIG. 29.—*Opening lower end of ditch for experimental drain at Sunnyside, Wash., showing partially excavated trench. Note amount of vegetation as compared with that in Fig. 27*

FIG. 30.—*Upper end of site of experimental drain at Sunnyside, Wash., showing lack of vegetation and heavy alkali crust on surface of ground. The salts appear much more concentrated on the surface at the upper end than at the lower end. While there are scattered deposits of salts on the surface over the site, conditions do not appear as bad as upon some of the other projects*

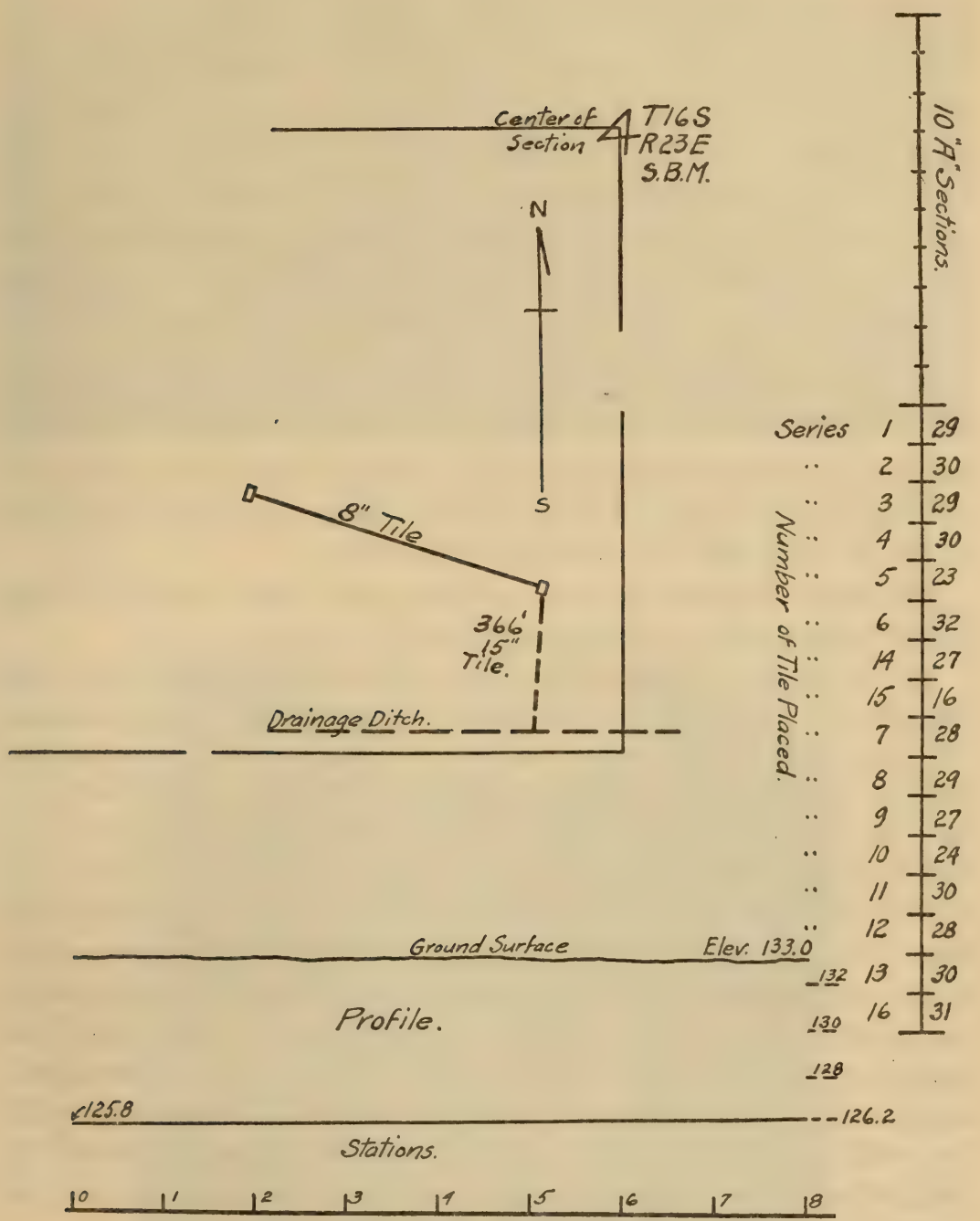

FIG. 31.—*Showing location, plan, profile, and arrangement of experimental drain tile at Yuma, Ariz.*

of drainage investigations, Department of Agriculture. This land had previously been irrigated and cultivated, but was later abandoned on account of the concentration of alkali on the surface and in the upper part of the soil. At the time the experimental tile were placed the surface was entirely covered with a thick white coating of alkali salts, as shown in the accompanying photographs. (See Figs. 37 and 38.)

The trench was excavated to a depth of 5½ to 6½ feet, the lower portion being very wet and mucky, requiring heavy sheeting and bracing which interfered greatly with the work of excavation and made progress very slow. (See Fig. 39.) The tile were laid on a grade of 0.3 foot per hundred feet.

The drain empties into a large wood silt basin which is a part of the system of drains of an adjacent 10-acre tract. Although the line is straight without bends, another basin was placed at the end of the tenth "A" section and also one at the upper end to aid in observing the working of the drain.

The total breakage in this shipment was nine tile, four being found broken while unloading the car.

(*h*) MONTROSE, COLO.—The point selected for placing the tile was about 12 miles from Montrose on "seep" land near milepost No. 6 and below the level of the South Canal on the Uncompahgre Project of the United States Reclamation Service. The soil consists of adobe and shale. This shale becomes very hard when dry and is difficult to excavate. The upper end of the tile line was entirely through shale. The amount of water flowing in the bottom of the trench was small, being as great near the upper end as at the outlet, indicating that most of the seepage occurs through the shale. Seepage was small in amount because the canal had been emptied previous to the excavation of the ditch for the experimental drain, but during the summer months the seepage should be considerably increased, as the change from concrete-lined to the unlined canal, whose maximum capacity is 1300 second-feet, is made opposite the upper end of the tile line.

The breakage of tile at this point was the maximum, 22 tile being damaged in the railroad and wagon haul. A 12-foot wooden box was placed at the outlet and wooden silt boxes at the two

FIG. 32.—*View from upper end of opened ditch for experimental drain at Yuma, Ariz., showing tile laid along the ditch ready for placing. There is only little alkali salt visible on the surface at this site, and conditions do not appear to be as severe as on many of the other projects, although the salts perhaps are of the worst character*

FIG. 33.—*View of opened ditch at Yuma, Ariz., showing heavy flow of seepage water in the bottom; also the method*

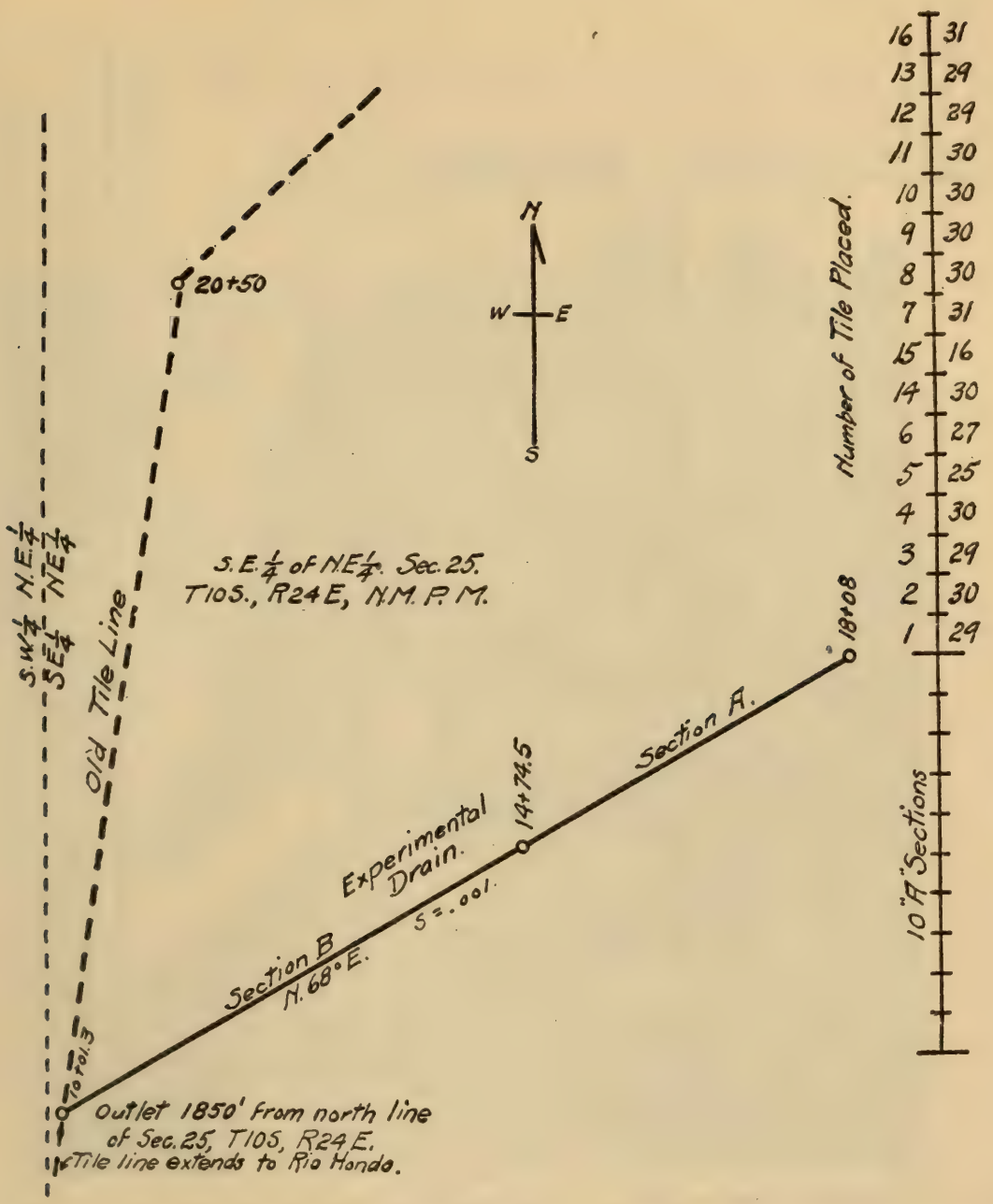

FIG. 34.—*Showing location, plan, and arrangement of experimental drain tile at Roswell, N. Mex.*

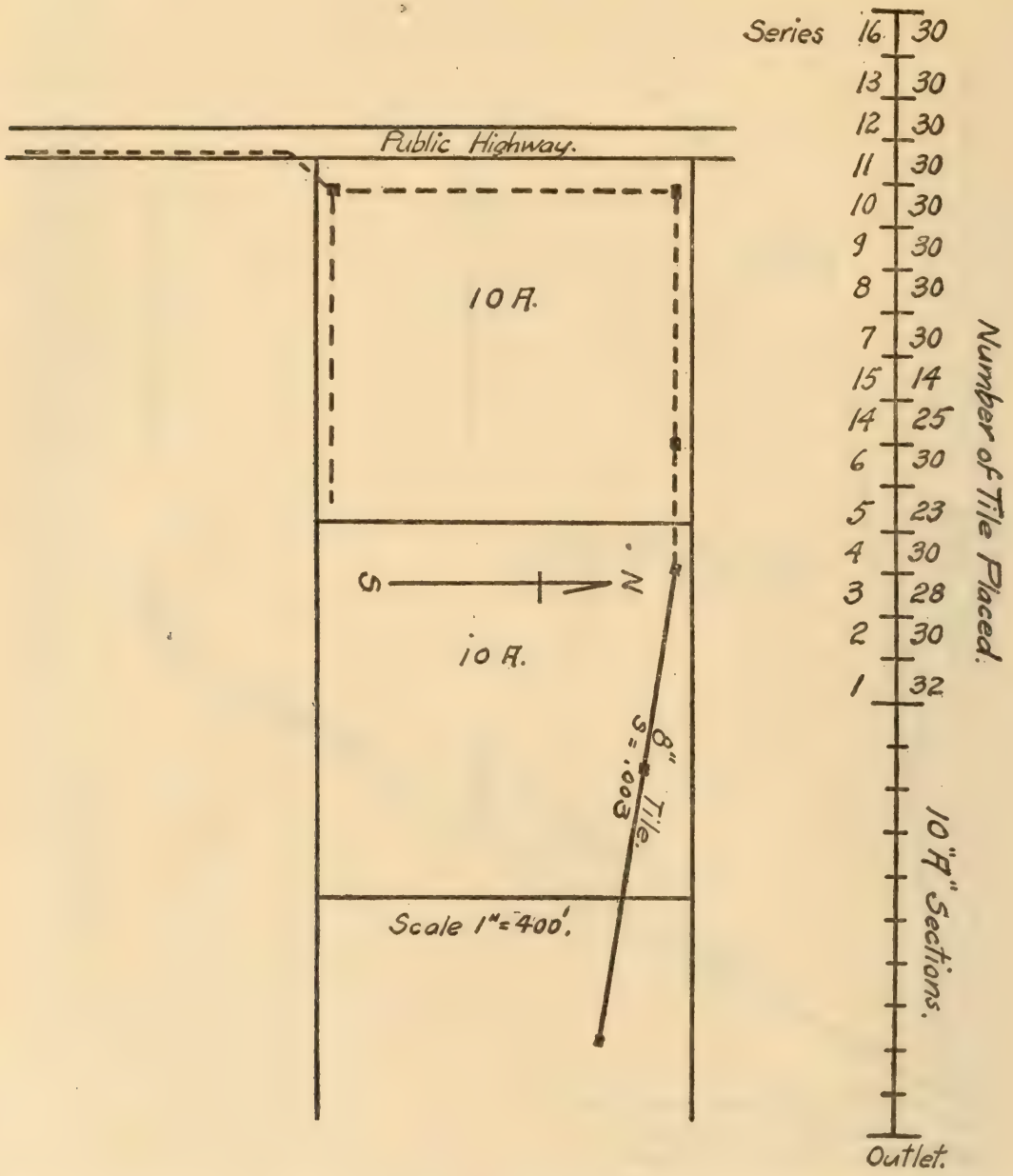

FIG. 36.—*Showing location, plan, and arrangement of experimental drain tile at Grand Junction, Colo.*

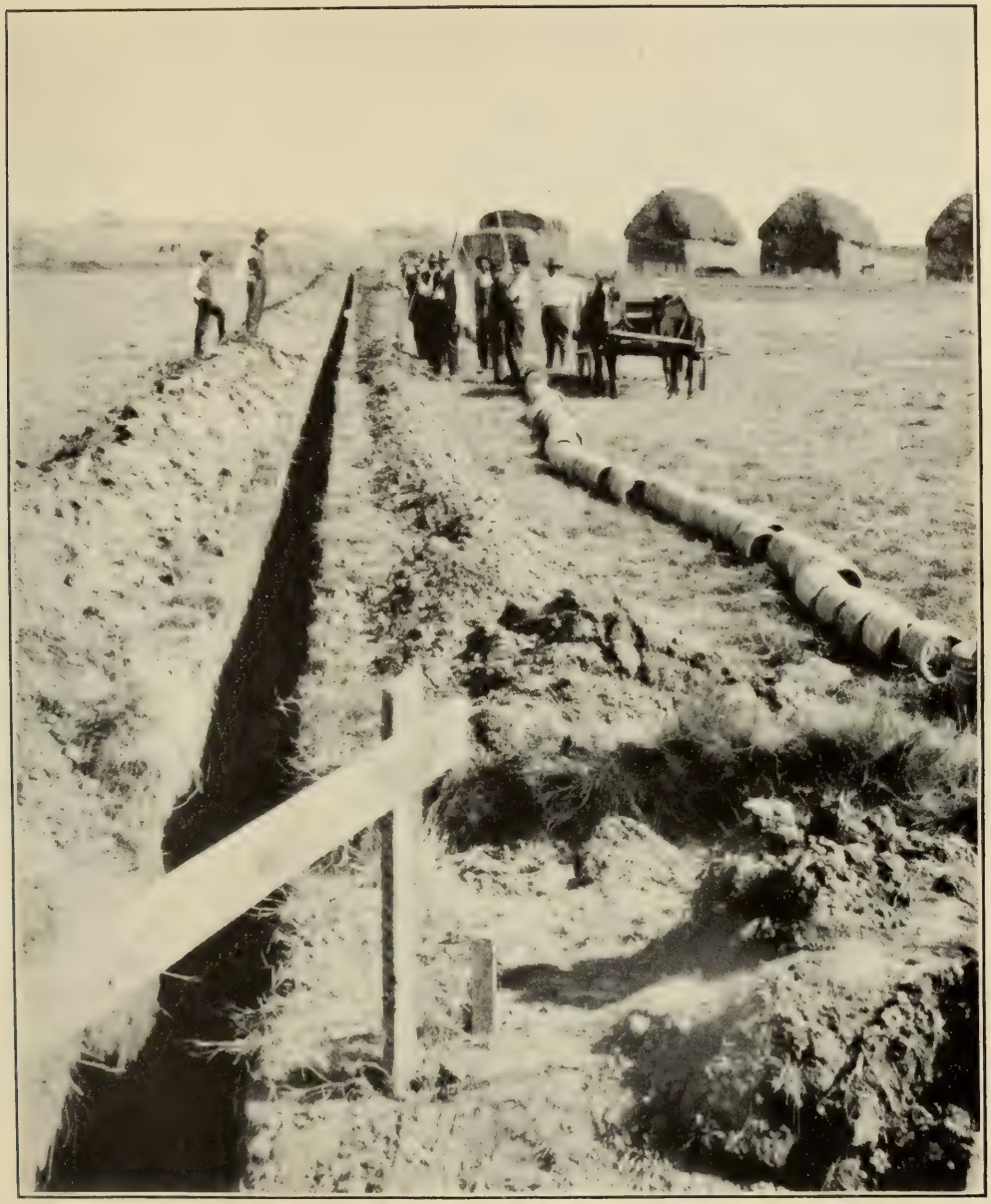

FIG. 35.—*View from lower end of opened ditch for experimental drain at Roswell, N. Mex., showing tile strewn ready for placing. Note the entire trench is partly excavated and banks are vertical. The concentration of salts is not as great at this project as at some of the others*

FIG. 37.—*View of site of experimental drain at Grand Junction, Colo., showing extremely heavy concentration of alkali salts on the surface of the ground. There is practically no vegetation other than alkali weed. Observe the salts are more concentrated on the high spots*

FIG. 38.—*Site of experimental drain at Grand Junction, Colo., showing heavy alkali deposit. The tile have been strewn ready for placing. Note lack of vegetation*

FIG. 39.—*Opened ditch for experimental drain at Grand Junction, Colo., showing the difficulties encountered in placing the tile. Observe the caving banks and timber bracing required*

angles, at stations 2+60 and 5+35. From stations 1+92 to 2+42 and 2+75 to 3+07 the tile were laid on boards in the bottom of the trench. The location of this drain is shown in Figs. 40, 41, and 42.

(*i*) COLUMBIA, MO.—The experimental drain at Columbia was placed on land belonging to and being farmed by the University of Missouri Agricultural School, about one-half mile south of the campus. The line, which has a total fall of about 24 feet, follows the line of a small channel which has been cut by surface water. The depth of the tile below the surface is small, as shown in Figs. 43 and 44, but it is sufficient to protect the line from frost action. The upper 12 or 15 inches is black soil and rather easy to dig, with the exception of a short length through the ridge at station 2+00, where some rocks were found. The soil was moist, but no stream of water was developed during the trenching. A wooden-box outlet was placed at the lower end where the earth covering was shallow.

The total breakage in the shipment of tile to this point was 22.

(*j*) CROOKSTON, MINN.—The tile shipped to Crookston were installed in a 40-acre tract of pasture land, which is part of the land belonging to the "Northwest Agricultural School" of the University of Minnesota, which is located about 1½ miles north of Crookston. This region is very flat and has very little natural surface drainage, being made up mainly of small ridges and depressions varying only a few feet in elevation. The flatness of the country, of which this farm is one of the lowest areas, is shown by the results of a topographical survey, which indicates that in the 476 acres included in this farm the greatest difference in elevation is about 2 feet.

The soil is mainly a clayey loam, the upper few inches being black, the lower sections yellow, but of about the same composition. The black soil appears to be deeper in the depressions. Scattered deposits of alkali salts can be found in the elevations. At the time the trench was dug the soil was quite moist and sticky, and was removed from the spade with difficulty. The lower foot was harder and drier and even more difficult to dig.

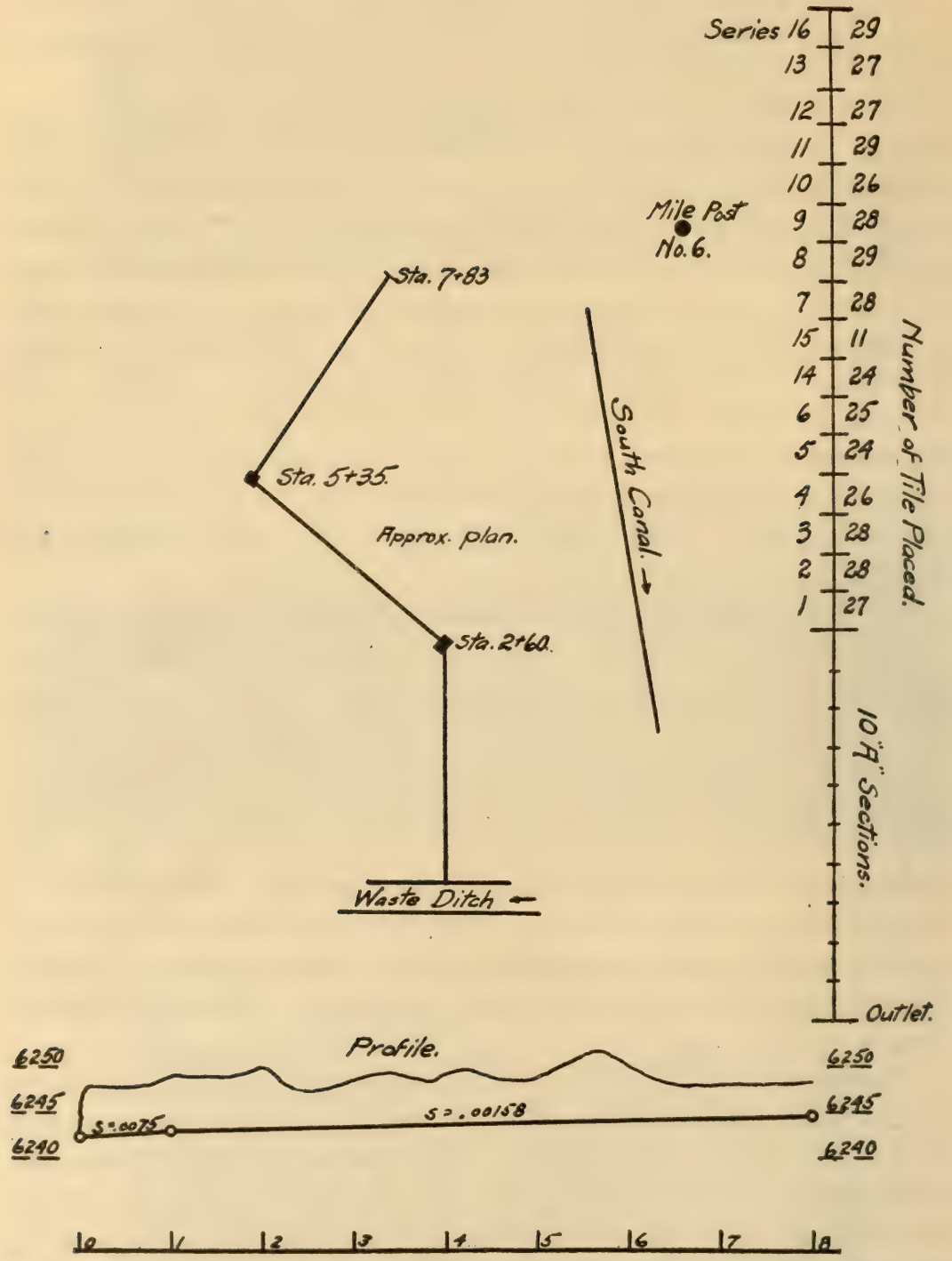

FIG. 40.—*Showing location, plan, profile, and arrangement of experimental drain tile at Montrose, Colo.*

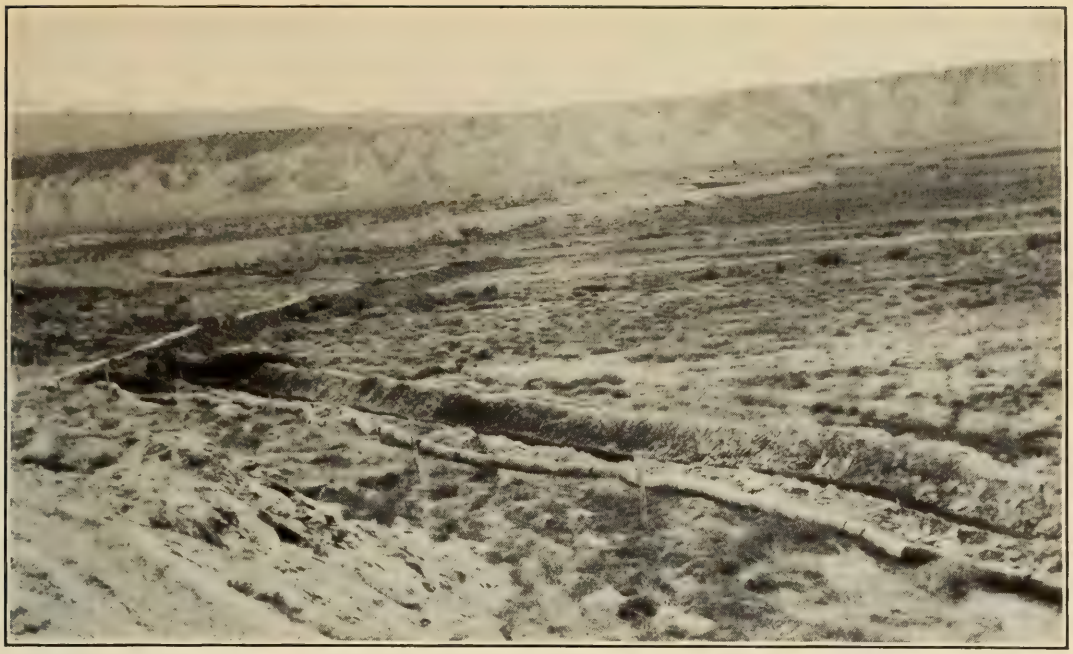

FIG. 41.—*View from upper end of site of experimental drain at Montrose, Colo., showing the opened ditch and the distribution of the tiles just previous to placing. Observe hard shale excavated at upper end to the right in picture*

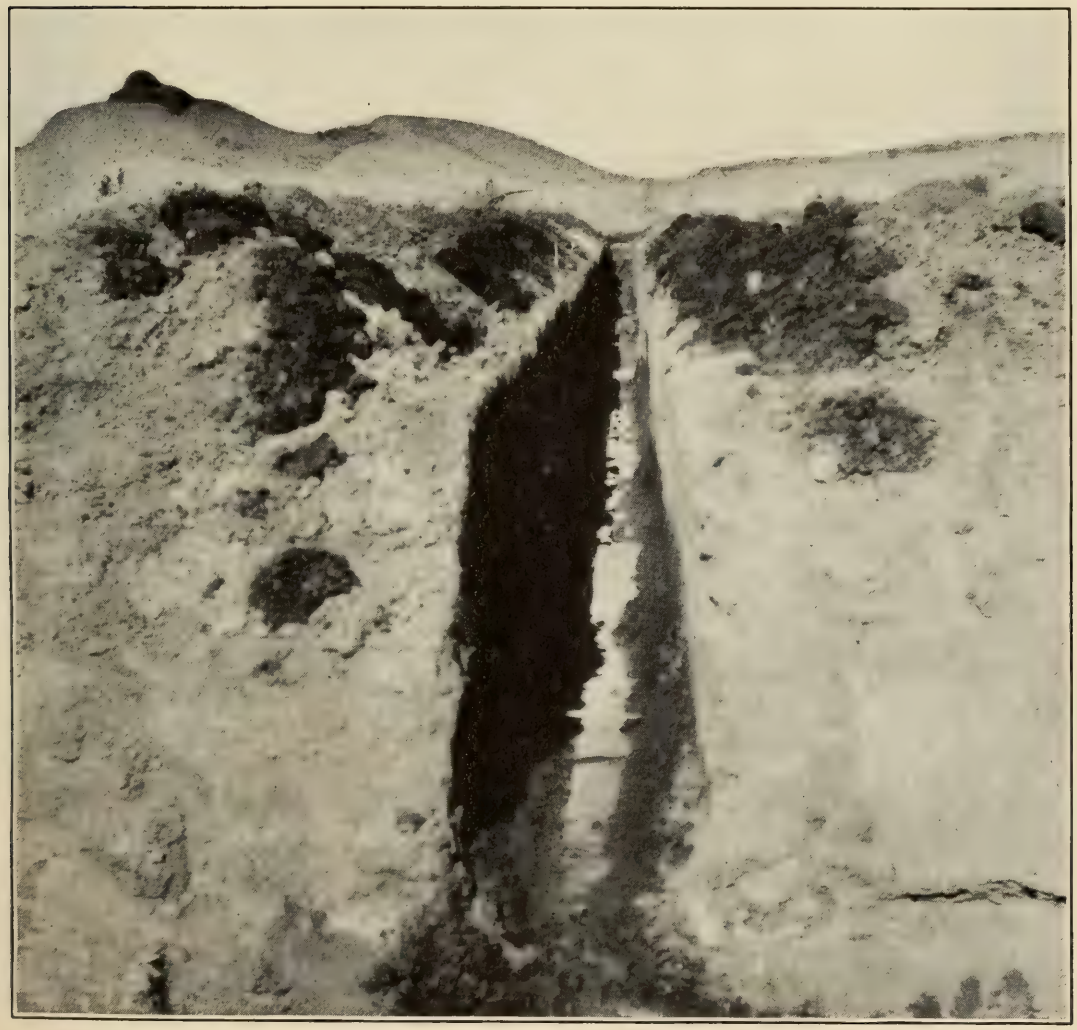

FIG. 42.—*Lower end of opened ditch for experimental drain at Montrose, Colo., showing depth of completed trench, flow of seepage water, and alkali salts on surface of soil where partially dried in the foreground*

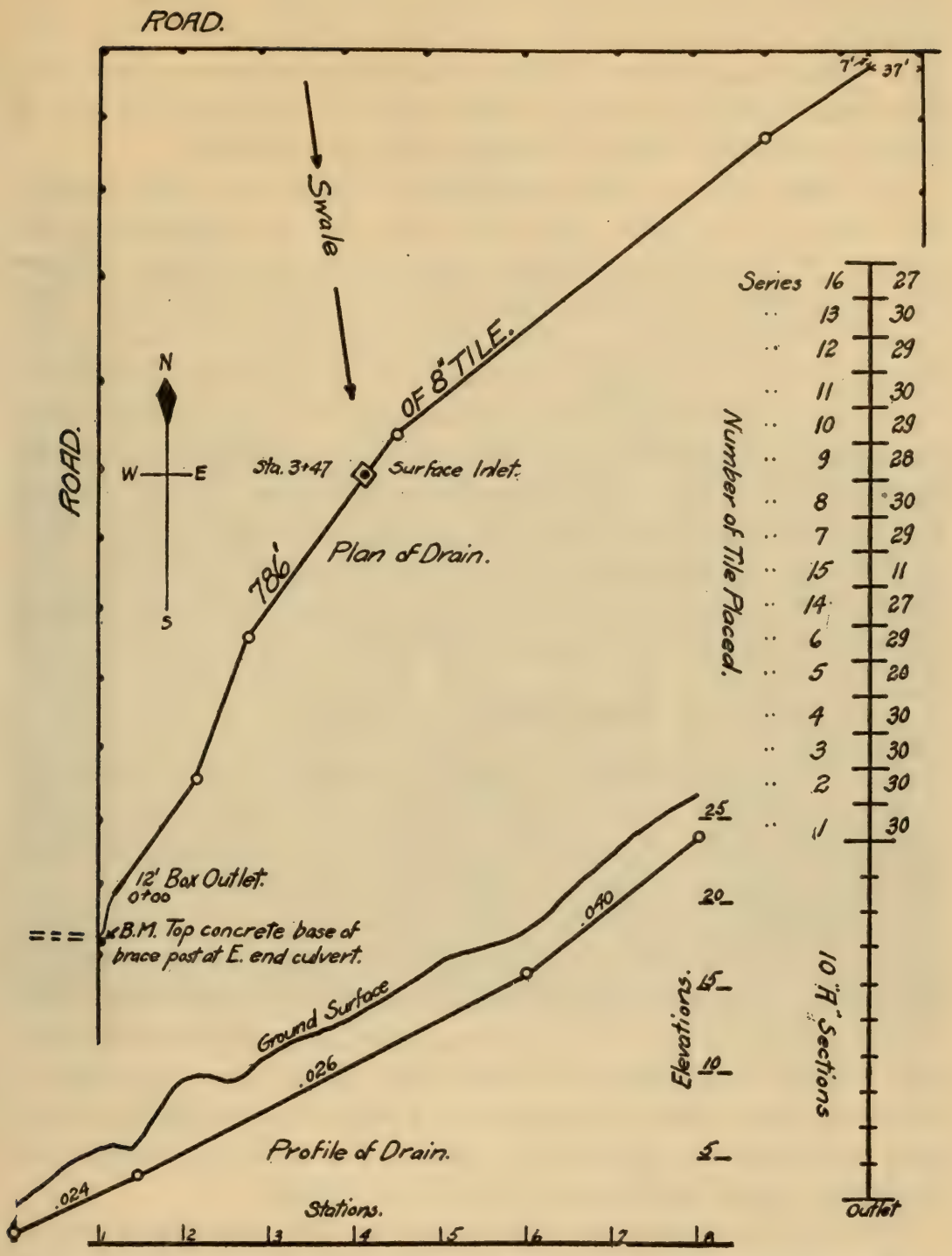

FIG. 43.—*Showing location, plan, profile, and arrangement of experimental drain tile at Columbia, Mo.*

As shown in Fig. 45 the tile were placed quite shallow, with a uniform fall of 0.8 foot in the length of 800 feet. A wooden box emptying into an open ditch was placed at the outlet. (See Fig. 46.) There was no flow of water at the time the tile were installed. The total breakage in tile in this shipment amounted to six, of which three were broken in being hauled to the ditch.

(*k*) AMES, IOWA.—A car containing 48 tile of each series, excepting series 15, of which there were only 42, was shipped to the campus of Iowa State College, Ames, Iowa, for storage. These tile were piled on wooden strips so as to keep them above the surface of the ground. A more careful account was made of the breakage here than had been made of the previous shipments. Although no packing of any kind was used and the tile were piled to a height varying from four high at the ends to two high at the doorway of the car, only three tile were broken. When the car was opened, the tile were found arranged just as placed at the time of loading. The breakage was confined to the lower layers near the car sides, indicating that the damage was due to the wedging of the tile, caused by movement of the car sides.

V. TESTING OF TILE

The first physical tests of the tile were made in 1914, about one year after the tile were placed. A representative of the Bureau visited all projects, where two tile of each type were removed from each drain and tested immediately upon removal.

A small portable machine was designed (Fig. 47) which could be transported to the site of the drains. This machine with all accessories and trunk for carrying weighed 170 pounds. The machine is of 3800-pound capacity, of the three-edge bearing type, and consists essentially of a steel angle iron frame supporting a hydraulic press which is operated by a hand lever through a worm gear and screw for applying the load. The load is recorded on a hydraulic gauge which can be read to 5 pounds.

The tile were uncovered and taken from the ditch one or two at a time, cleaned, measured, and tested immediately. Notes were made on the length and thickness of the tile at each end; also its condition if in any way abnormal. The tile were placed in the

FIG. 44.—*Lower end of experimental drain, Columbia, Mo., showing shallow installation of tile necessary on account of high outlet*

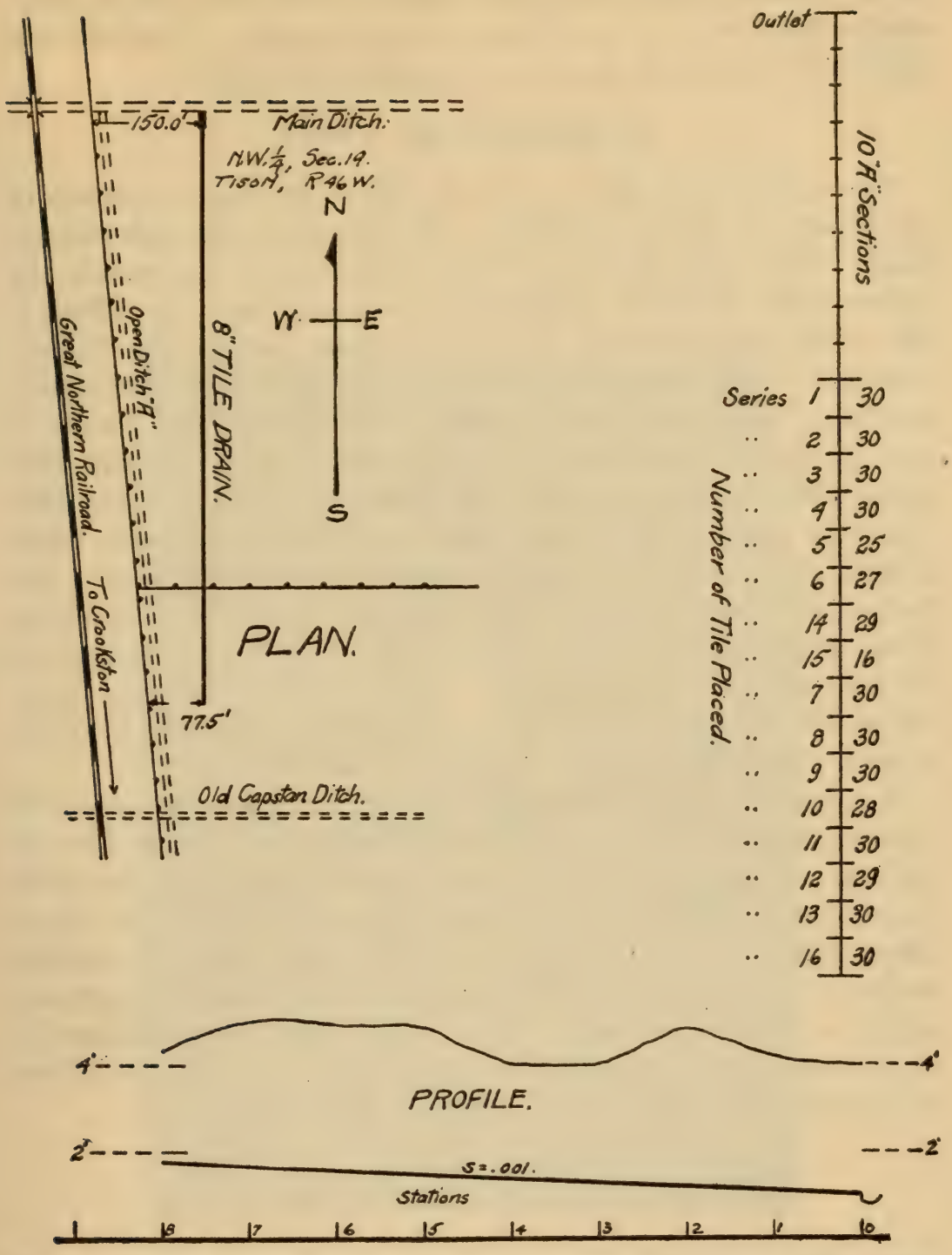

FIG. 45.—*Showing location, plan, profile, and arrangement of experimental drain tile at Crookston, Minn.*

machine in the same relative position as found in the ditch, care being taken to obtain a uniform bearing on all edges and to operate the hand lever at as uniform a rate as possible. The load was applied at the rate of about 1500 pounds per minute.

VI. RESULTS OF TESTS

The results of all tests of the tile after one year's exposure in alkali soils are given in Table 8. To determine the approximate loads which these tile would have withstood in the trench the results given should be multiplied by the constant 1.50, which is the factor recommended by the American Society for Testing Materials. The results as a whole are quite uniform and compare favorably with other tests of drain tile. Occasionally results of tests of similar tile differ by 30 or 40 per cent, but usually they agree within a few per cent. It should be borne in mind that these tile are exposed to abnormal conditions, which may cause a variation in results of tests of apparently similar tile only a few feet apart in the same ditch. No general conclusions should be drawn from the results of this investigation until it has progressed for several years and tests have been made of a sufficient number of tile of each type to confirm beyond question the behavior of each particular type.

A summary of the results is given in Table 9. The results of tests included in Table 9, are shown diagrammatically in Figs. 48 and 49. It should be emphasized that the breaking tests alone should not be taken as an index of the resistance of the tile to alkali action, as some of those which had a normal or only slightly reduced strength showed evidence of alkali action by softened edges or cracked surfaces. Where such action has been noted it is possible another year or two of exposure may cause the failure of the tile although this need not necessarily result.

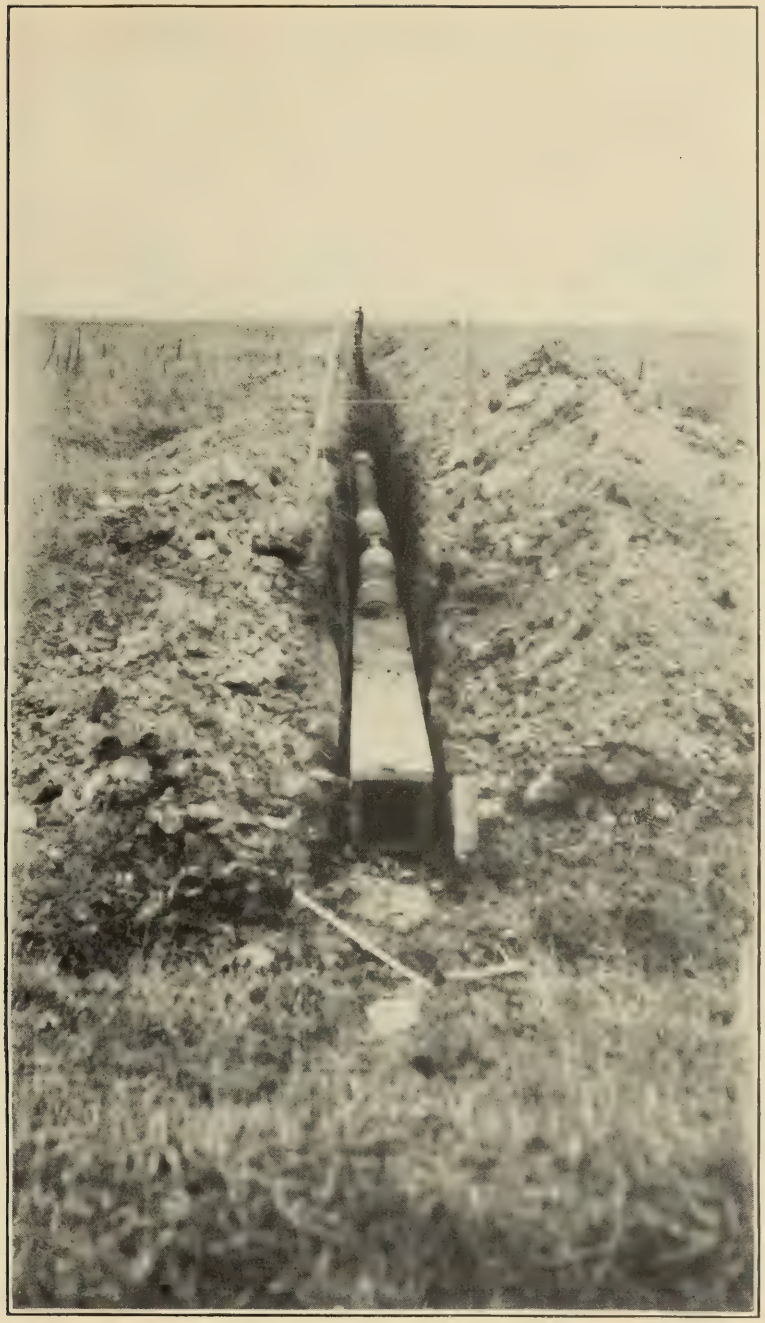

FIG. 46.—*Lower end of experimental drain at Crookston, Minn., showing shallow installation of tile with box at outlet to prevent tile being washed out*

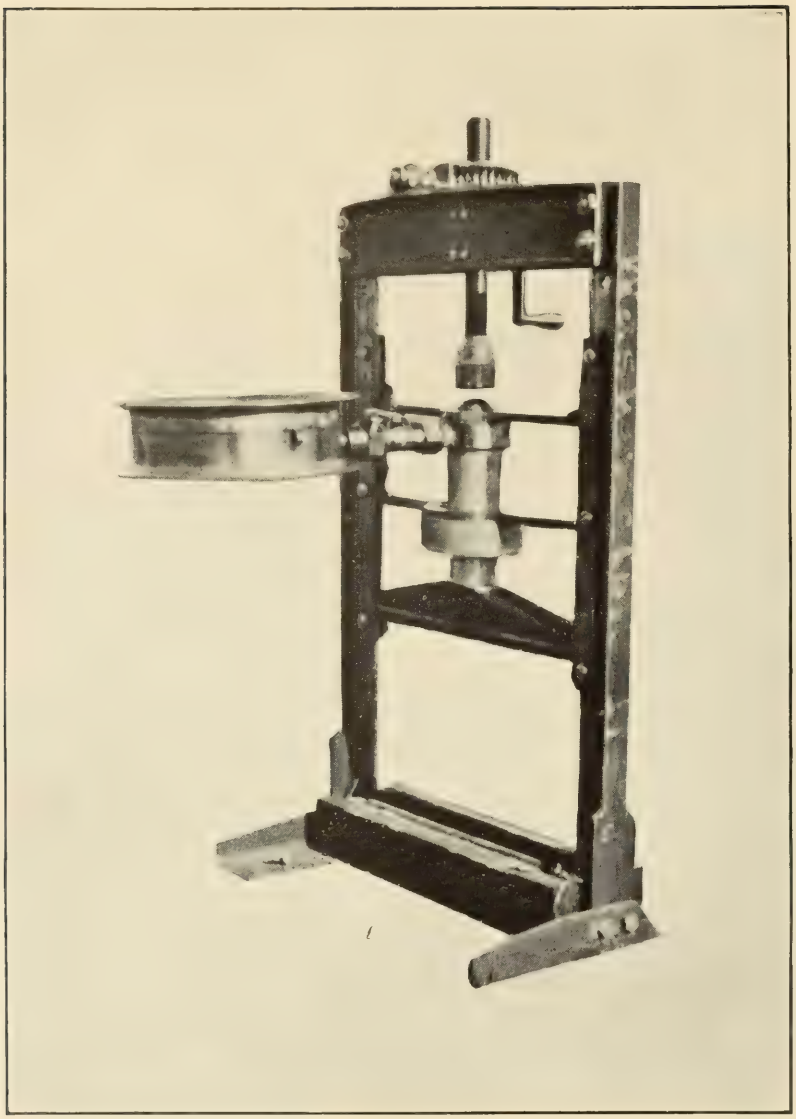

FIG. 47.—*Portable tile-testing machine of three-edge bearing type used in testing experimental tile at the site of the drain. The pressure applied to the tile through the worm gear and screw is measured in the hydraulic gauge which is attached to the ram*

TABLE 8

Complete Results of Tests of Experimental Cement Drain Tile (1914)

[Total breaking load in pounds]

Exposure	Location	Tile series No. —															
		1		2		3		4		5		6		14		15	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Atmosphere.[a]	Ames, Iowa...	2825 2895 3195		2425 2895 2660		2395 2130 1990		1955 2045 2950		2905 3220 3105		2140 3150 2320		2030 2670 2275		1275 2045 1530	
Fresh water.	Columbia, Mo	2705	2670	2600	2385	2480	2690	2725	2615	2140	2555	2535	2750	2555	2340	1615	1515
	Crookston, Minn.	2579	2759	2748	3085	2770	3231	[b]2394	2951	2181	2592	2883	2523	2782	2748	1319	1770
Alkali water.	Garland, Wyo	3390	3175	3030	2885	1945	[c]3365	2680	2750	2645	2750	2340	1910	2770	2435	1595	1375
	Fort Shaw, Mont.	2780	2470	2490	2570	2680	2525	1825	2350	1900	3105	[d]2545	[d]3715	2670	2995	1385	1680
	Sunnyside, Wash.	2645	2460	3005	3285	2570	[b]1980	2320	2840	2415	2660	2350	1910	2360	2635	1375	1375
	Yuma, Ariz...	2570	3420	2860	3120	2350	2160	2500	2375	2075	2350	1910	2340	2535	2660	1715	1550
	Roswell, N. Mex.	2385	3050	3590	2690	2840	2490	2645	2425	2470	3230	2985	[b]2010	2750	2525	1750	1470
	Montrose, Colo	2870	2715	3075	3030	2200	2360	2940	3500	3150	3150	2245	2795	2705	2905	[e]1220	1220
	Grand Junction, Colo.	2590	2670	2815	2975	2885	[f]1375	2130	2555	2055	2115	2045	2960	2265	3175	[e]1625	[e]1855
	Huntington, Utah.	[i]2435	2105	3330	3580	1530	1825	3465	2985	2770	2645	[g]1485	[h]1440	2770	2905	1725	2105

[a] Tests were made at Ames following a heavy rain to which the tile had been exposed.
[b] Fractured surfaces showed poor tamping of walls.
[c] Heavy, crusty, white deposit on outer bottom surface. Apparently did not penetrate into wall.
[d] White deposit on outer surface near one end of tile.
[e] Soft spot on outer surface at end of tile.
[f] Fractured surface white.
[g] Circumferential crack apparent after breaking.
[h] Two longitudinal cracks and circumferential cracks at ends.
[i] Long crack previous to testing. Crack placed so as to be at eighth point in machine.

TABLE 8—Continued

Exposure	Location	Tile series No. — 7 a	7 b	8 a	8 b	9 a	9 b	10 a	10 b	11 a	11 b	12 a	12 b	13 a	13 b	16 a	16 b
Atmosphere.[a]	Ames, Iowa	1265		940		1570		1540		1255		1100		1385		1185	
		1165		860		1485		1310		1120		1130		1185		1100	
		1385		1035		1945		1440		1360		1055		1450		1350	
Fresh water.	Columbia, M.	1210	1145	1075	970	1530	1705	1695	1870	[b]1200	1200	1145	1200	1460	1485	1000	1155
	Crookston, Minn.	1517	1417	950	1044	1660	1506	1770	1857	1275	1439	920	1154	1472	1406	1000	880
Alkali water.	Garland, Wyo.	1200	1605	770	820	1570	1440	1145	1090	1255	1275	570	730	1285	1000	660	720
	Fort Shaw, Mont.	1185	1310	1185	910	1625	1485	1550	1515	1495	1360	1045	980	1045	1375	1020	940
	Sunnyside, Wash.	900	1320	980	990	1870	1585	1640	1750	1110	1595	1035	1035	1625	1265	1055	950
	Yuma, Ariz.	1505	1255	1054	1090	1715	1650	1640	1980	1340	1395	910	1055	1185	1200	1000	1100
	Roswell, N. Mex.	1175	1470	980	1100	1450	1660	1605	1185	1495	1375	1255	880	1790	1120	1145	1010
	Montrose, Colo.	1405	1340	1000	960	1910	1495	1630	1055	1265	1130	1000	1000	1395	1595	490	1065
	Grand Junction, Colo	1295	1220	840	910	1175	1495	1295	1310	1310	1340	1035	1265	1440	1065	760	(c)
	Huntington, Utah.	1570	1505	1075	1120	1920	1945	1570	1955	1695	1450	1185	1090	1680	1295	840	1075

[a] Tests were made at Ames following a heavy rain to which the tile had been exposed.

[b] Exact breaking load not noted; approximately 1,200 pounds.

[c] Tile badly swollen and cracked. Not broken in machine.

TABLE 9

Results of Tests of Experimental Cement Drain Tile (1914)

[Average total breaking load in pounds.]

Exposure	Location	Tile series No.—																Average of all tile
		1	2	3	4	5	6	14	15	7	8	9	10	11	12	13	16	
Atmosphere...	Ames, Iowa.....	2972	2660	2172	2317	3077	2537	2325	1617	1272	945	1667	1430	1245	1095	1340	1212	1866
Fresh water...	Columbia, Mo.....	2687	2492	2585	2670	2347	2642	2447	1565	1177	1022	1617	1782	1200	1172	1472	1077	1871
	Crookston, Minn..	2670	2917	3000	2672	2385	2705	2765	1545	1465	997	1582	1813	1357	1037	1437	940	1955
Average.....		2678	2704	2792	2671	2366	2673	2606	1555	1321	1009	1599	1797	1278	1104	1454	1008	1913
Individual maximum.		2760	3085	3230	2950	2590	2885	2780	1770	1515	1075	1705	1870	1440	1200	1485	1155	.....
Individual minimum.		2580	2385	2480	2394	2140	2525	2340	1320	1145	950	1505	1695	1200	920	1405	880	.....
Alkali water...	Garland, Wyo.....	3282	2957	2655	2715	2697	2125	2602	1485	1402	795	1505	1117	1265	650	1142	690	1818
	Fort Shaw, Mont..	2625	2530	2602	2087	2502	2630	2832	1532	1247	1047	1557	1532	1427	1012	1210	980	1834
	Sunnyside, Wash.	2552	3145	2275	2580	2537	2130	2497	1375	1110	985	1727	1695	1352	1035	1445	1002	1840
	Yuma, Ariz.....	2995	2990	2255	2437	2212	2125	2597	1632	1380	1072	1682	1810	1367	983	1192	1050	1861
	Roswell, N. Mex..	2717	3140	2665	2535	2850	2497	2737	1610	1322	1040	1555	1395	1435	1067	1455	1077	1943
	Montrose, Colo....	2797	3052	2280	3220	3150	2520	2805	1220	1372	980	1702	1342	1197	1000	1495	777	1931
	Grand Junction, Colo.	2630	2895	2130	2342	2085	2502	2720	1740	1257	875	1335	1302	1325	1150	1252	760	1769
	Huntington, Utah.	2270	3455	1677	3225	2707	1462	2837	1915	1537	1097	1932	1762	1572	1137	1487	957	1939
Average.....		2734	3020	2317	2643	2593	2249	2703	1564	1328	986	1624	1494	1368	1004	1335	912	1868
Individual maximum.		3420	3590	3365	3500	3230	2985	3175	2105	1605	1185	1945	1980	1695	1265	1790	1145	.....
Individual minimum.		2105	2490	1375	1825	1900	1440	2265	1220	900	770	1175	1055	1110	570	1000	490	.....

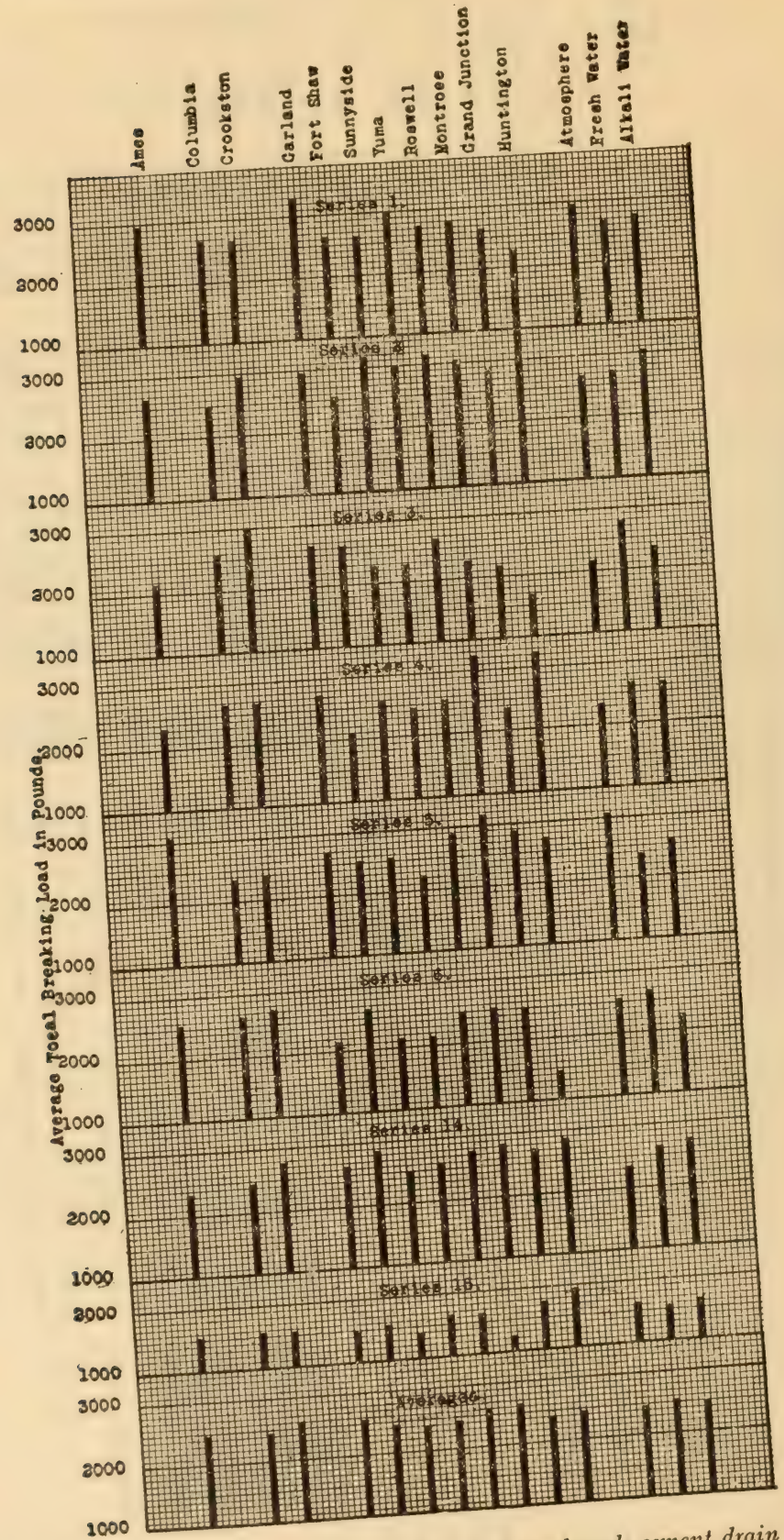

FIG. 48.—*Results of first year's tests of hand-made cement drain tile. (See Table 9 for detailed results)*

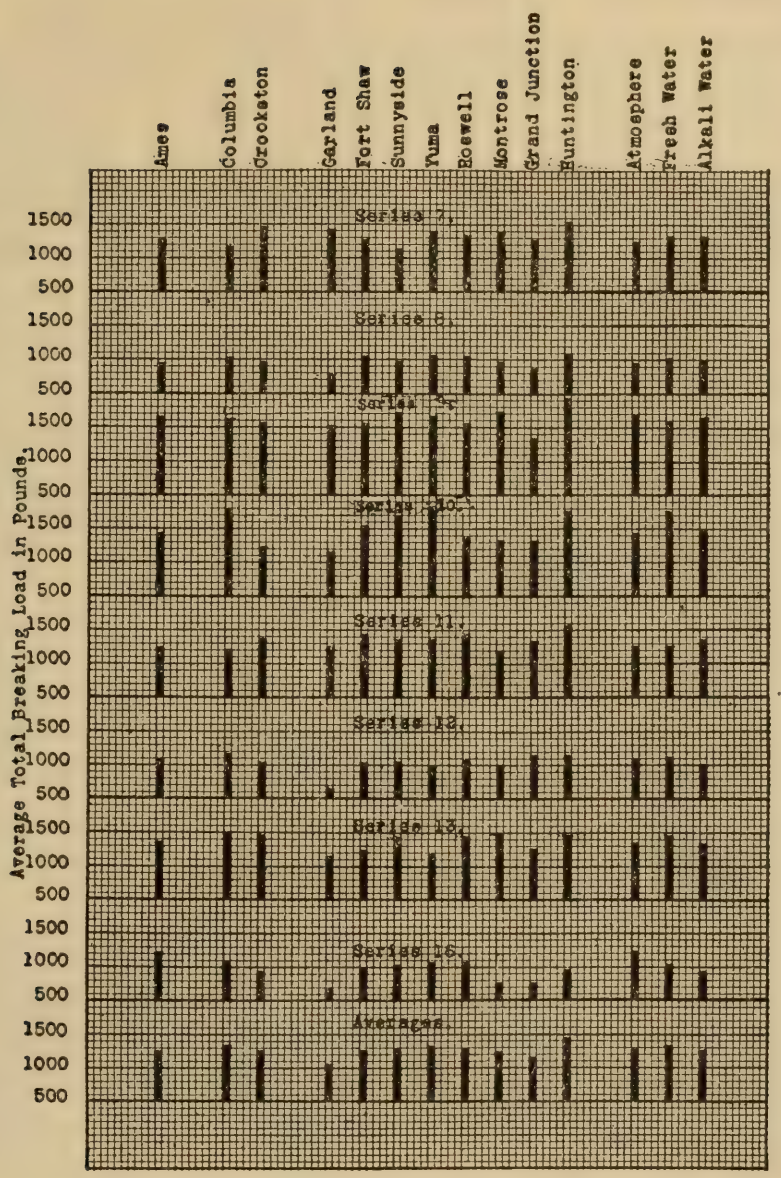

FIG. 49.—*Results of first year's tests of machine-made cement drain tile. (See Table 9 for detailed results)*

The variations in results of the same mixtures at the same or several points may also be due in part to the nonhomogeneity of the material, due in most part to nonuniform or insufficient "packing" in the machine, or "tamping" by hand. With the same materials the two factors which enter into the strength of the product are "richness" or proportion of cement and the fabrication or process of manufacture. A rich mixture alone will not insure a product of good quality. The low strength results obtained in a number of cases of the richer mixtures can be explained by poor tamping, especially in the handmade tile, in whose broken surfaces rings of untamped material were apparent. Even though extra care is taken in the tamping there is certain to be some variation in density which will affect the strength.

The great majority of the tile were unaffected in any manner at any of the projects. At Sunnyside, Wash.; Yuma, Ariz.; and Roswell, N. Mex., it may be stated that none of the tile showed any abnormality whatever. At Garland, Wyo., the leanest mixtures, series 8, 12, and 16, showed reductions in strength considerably below the averages for these series at all points. Series 10 was also below the average, but the results are explained by the fact that the tile were completely saturated, an unusual condition for the tile in this series, which may be due to excessive porosity. At Fort Shaw, Mont., one tile each of series 4 and 5 showed reduced strength, but the remaining two of the same series were about normal.

At Grand Junction, Colo., the tile made of the leanest mixture (series 16) were swollen and cracked, as shown in Fig 50. The tile made of sand-cement, series 15, while of normal strength showed a softening at the edges and several square inches of one of the tile was similarly affected although the breaking strength was normal.

At Huntington, Utah, the tile of series 6 appeared to be affected by the alkali. Although these tile withstood loads of over 1,400 pounds, there were a number of longitudinal and circumferential cracks apparent before testing and the fractured surfaces appeared white.

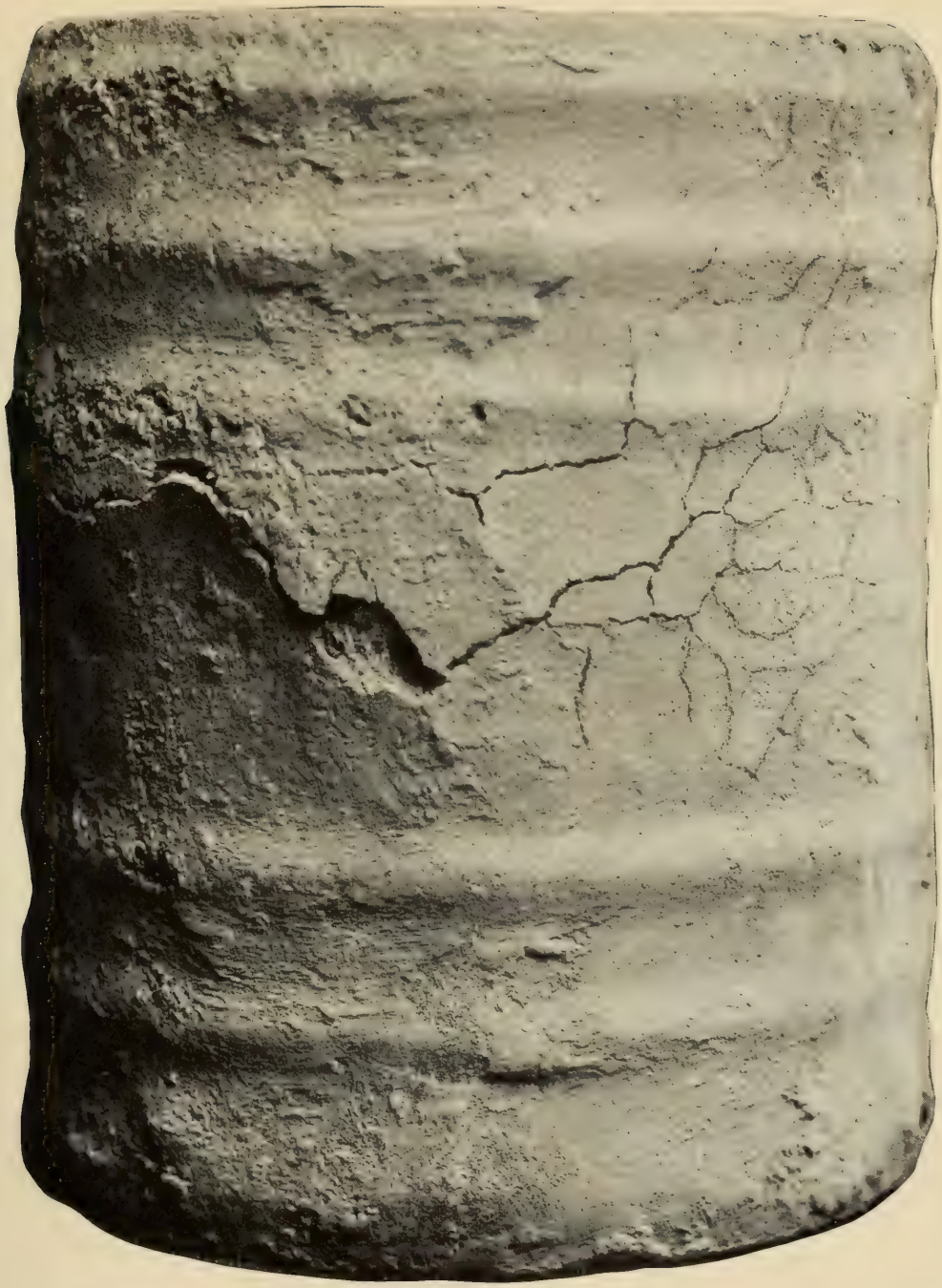

FIG. 50.—*Swollen and cracked tile of series 16 after one year's exposure at Grand Junction, Colo. The interior surface is cracked similar to the exterior*

At Montrose, Colo., the tile of series 15 appeared to have been affected by alkali. On one of the tile the concrete at one end was softened, apparently due to alkali, and both failed under comparatively small loads. The result obtained for tile 16a was abnormal, while that of 16b was rather above the average for this series. The early failure of the former may have been due to cracks which were overlocked at the time the tile was placed the year previous.

The absorption of moisture by the walls of the tile of the various series was noticeable at the different projects. The apparent amount of absorption varied with the amount of water present in the soils at the various points, and it was found that some of the series would be apparently saturated where the ground was barely moist while other series were apparently only slightly damp, even where the drain was filled with mud and water. Of the handmade tile and under the worst conditions series 2 was, with very few exceptions, found to be slightly damp, as indicated by the appearance of the fractured surfaces. This difference is not alone due to the variation in the proportions of the cement, since series 3, 4, 5, and 6, the richest mixtures used, were nearly always found partially or completely saturated. The term saturated is indefinite and inexact, since the condition was determined only by observation, but was used to indicate a dark spongy appearance of the fractured surface common to water-soaked concrete. The tile of series 14, next to those of series 2, showed the smallest amount of absorption, while the tar-coated tile of series 5 and the tile of series 6, containing the ferrous sulphate, were usually found to show the greatest absorption. We have no explanation to offer for the saturation of the tile of series 5 and 6.

The absorption of the machine-made tile varied as the amount of cement contained in them. The tile of series 9 and 10 were usually found apparently dry or only partially saturated with a few wet spots in the fractured surfaces while the tile of series 8, 12, and 16, the leanest mixtures, were always found saturated. Some low results obtained may be partially due to higher porosity, which caused the tile to be saturated when tested. This condition would also tend to increase the danger of failure due to alkali action at a later period.

VII. CONCLUSIONS

The details of this investigation and the results of the first year's tests are published at this time because of their economic value in demonstrating to those who are now using or considering using cement drain tile that special care should be observed to employ only the best materials and good workmanship in its fabrication, and if these precautions are not observed failure will result if the drain is located in some of the more concentrated alkali soils similar to those found at Grand Junction, Colo., and Garland, Wyo.

Drain tile manufactured in a manner as herein described for series 2, 9, 10, 11, 13, and 15 of cement mixtures not leaner than one part cement to three parts of aggregate are apparently unaffected structurally when exposed for one year in operating drains in very concentrated alkali soils, similar to anv of those included in this investigation.

Drain tile made from cement mixtures leaner than one part cement to three parts of aggregate should not be used in localities where the character of the alkali and concentration are similar to that found at the site of the experimental drains at Grand Junction, Colo., Montrose, Colo., and Garland, Wyo., and it is possible that subsequent results will show that no leaner mixture should be used in any district where appreciable alkali is found.

Drain tile manufactured in the manner herein described of one part cement to four parts of aggregate, the leanest mixture used, is apparently unaffected structurally by exposure for one year in an operating drain in localities where the character of the alkali and the concentration are similar to those found at Fort Shaw, Mont.; Sunnyside, Wash.; Yuma, Ariz.; and Roswell, N. Mex.

Other than the above, no very general conclusions should be drawn from this investigation until the results of further tests are obtained. It is anticipated that this report will be amended from time to time as the results are available.

The Bureau would be pleased to receive information concerning the behavior of concrete exposed to strongly alkaline soil which may come to the attention of engineers or others interested in the use of concrete under these conditions.

WASHINGTON, February 6, 1915.

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 45

A STUDY OF SOME RECENT METHODS FOR THE DETERMINATION OF TOTAL SULPHUR IN RUBBER

BY

J. B. TUTTLE, Assistant Chemist

and

A. ISAACS, Laboratory Assistant

Bureau of Standards

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A STUDY OF SOME RECENT METHODS FOR THE DETERMINATION OF TOTAL SULPHUR IN RUBBER

By J. B. Tuttle and A. Isaacs

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I. PURPOSE OF INVESTIGATION

One of the most important problems in the chemical analysis of rubber compounds is the determination of total sulphur. Many investigators have worked on this subject, with the result that different laboratories have their own methods, and comparison of results obtained by these various methods is always difficult, and at times impossible.

This Bureau is now using in its routine analysis, the method of Waters and Tuttle.[1] In order to learn whether or not the methods for this determination, which have been recently published, were an improvement either in accuracy or time required over the one now in use, and, if not, to determine wherein these methods are faulty, the present investigation was undertaken.

[1] Bureau of Standards, Reprint 174; J. Ind. and Eng. Chem., 3, p. 734; 1911.

II. GENERAL CONSIDERATION

The determination of the total sulphur in rubber is far from being a simple problem, involving as it does the simultaneous determination of sulphur in a number of different substances. Sulphur may be found in vulcanized rubber compounds in any of the following forms:

1. Free sulphur.
2. Sulphur combined with rubber (i. e., vulcanized rubber).
3. Metallic sulphates, usually lead and barium.
4. Metallic sulphides, usually lead and zinc.
5. Sulphur compounds of fatty acids (from the so-called oil substitutes, or "factis").
6. Sulphur in bituminous substances ("mineral rubbers").

The first and second of these are always present, and the others may or may not be, according to the nature of the compound. Any method which has for its purpose the determination of the total sulphur must be adequate to determine any or all of these in widely varying amounts. In our experience in testing material for use in the Government departments, the total sulphur has varied from 1.5 to 25 per cent; the free sulphur from practically nothing to 10 per cent; and sulphur in metallic sulphates from nothing up to 6 per cent. The rubber content varied from 20 to 90 per cent, and the quality of the rubber varied from the best to the poorest. We have no quantitative data on the other sulphur-bearing components of rubber goods, but we are certain that they are frequently present and carry appreciable quantities of sulphur.

The almost universal use of litharge (in amounts sometimes 15 and even 20 per cent) in rubber mixings may have considerable bearing on the determination of sulphur by some methods, even though the litharge does not in itself contain sulphur. Its effect on the determination of total sulphur will be referred to later in the discussion of the results obtained by the methods investigated.

III. REVIEW OF RECENT METHODS

In connection with the previous publication on this subject from this Bureau,[2] a number of the methods in use at that time were investigated and discussed. Since then several new methods have

[2] Waters and Tuttle, loc. cit.

been proposed. Alexander's [3] method, involving the oxidation of the rubber with sodium peroxide, was recommended by Allen [4] as a "reliable rapid method." Spence and Young [5] worked on a variation of the electrolytic oxidation first suggested by Gasparini,[6] and afterwards developed by Hinrichsen.[7] Kaye and Sharp [8] proposed fusing the rubber directly with a mixture of zinc oxide and potassium nitrate. Ernst Deussen [9] offered a new idea in an attempt to determine only the free sulphur and the sulphur combined with the rubber. After decomposition with concentrated nitric acid and evaporating, he treated the residue with sodium carbonate and water and filtered, determining the sulphur in the filtrate colorimetrically. The Joint Rubber Insulation Committee [10] proposed a procedure for the complete analysis of rubber insulation material according to which the total sulphur is determined by fusion with a mixture of sodium peroxide and potassium carbonate. While this method was recommended for 30 per cent Para insulation compounds only, it is desirable to know whether it has a wider application. H. P. Stevens [11] suggested a method for correcting for the loss of volatile sulphur in the Henriques method by absorbing the gases from the determination in alkali and subsequently determining the sulphur thus absorbed. Utz [12] gave a review of the subject in which the method of Kaye and Sharp was compared with that of Frank and Marckwald.[13] He considered the two methods of equal value.

There are two general methods for determining sulphur in organic compounds which have been used to determine the sulphur in rubber, viz, the Carius and the bomb methods. These are so well known that description at this time is unnecessary. Both of them are considered adequate to determine the total sulphur when modified to suit the conditions peculiar to rubber. Such modifi-

[3] Gummi Ztg., **18**, pp. 729–730; 1904.
[4] Allen's Commercial Organic Analysis, 4th ed., Vol. IV, p. 140; 1911.
[5] J. Ind. & Eng. Chem., **4**, p. 413; 1912.
[6] Gazzetta Chim. Ital., **37**, II, pp. 426–461; 1907.
[7] Chem. Ztg., **33**, p. 735; 1909.
[8] India Rubber J., **44**, p. 1189; 1913.
[9] Zs. Angew. Chem., **24**, p. 494; 1913.
[10] J. Ind. & Eng. Chem., **5**, p. 78; 1914.
[11] Analyst, **39**, p. 74, 1914; and India Rubber J., **47**, p. 785, 1914.
[12] Gummi Ztg., **28**, pp. 631–632; 1914.
[13] Gummi Ztg., **17**, p. 71; 1903.

cations, however, are time-consuming and render these methods undesirable for the routine analysis of rubber goods. It was therefore not considered necessary to give analytical data in this paper.

IV. SAMPLES

Even when the assumed total sulphur content is given, this information is not sufficient to enable one to judge the efficiency of the method, since some methods will give low results with materials containing much free sulphur. For the proper interpretation of the results by any method the entire composition of the samples used, at least as far as the sulphur-bearing constituents are concerned, should be known and reported.

The samples used in this investigation are described in the following table:

Composition of Samples

[The figures given below are approximate percentages only]

Sample	Description	Rubber content	Total S	Free S	Mineral fillers
A	Insulation	30 fine Para	5.0	0.5	18 barytes.
B	Suction hose	40 high grade	6.0	.5	18 barytes.
C	Special	48 fine Para	[a] 4.25	.6	16 barytes, 16 litharge.
D	Insulation	28.5 fine Para	1.75	1.00	4 litharge.
E	Rubber bands	93 high grade	5.0	2.7	2 litharge.
F	Special	42 coarse Para	[a] 8.1	4.0	30 sublimed lead, 5 litharge.
G	Gasket	55 poor quality	12.0	8.0	2 barytes, 2 litharge.
H	White tubing	20 poor quality	21.0	9.0	36 barytes.

[a] The amount of sulphur added as such in samples C and F was 2 per cent and 5.4 per cent, respectively.

Sample A was one of the samples used in the investigations of the Joint Rubber Insulation Committee. Samples B, E, G, and H were taken from deliveries on various Government contracts.[14] Sample D was prepared especially for the investigations of the analytical committee of the Rubber Section of the American Chemical Society. Samples C and F were specially prepared by one of the authors (J. B. Tuttle) at the factory of the Voorhees Rubber Manufacturing Co., at Jersey City, N. J., for the purpose of investigating the determination of total sulphur. Great care was taken in the weighing and mixing. The composition was chosen so

[14] In this connection it will be of interest to note that G was taken from a delivery offered on a contract calling for 50 per cent fine Para rubber and not over 3 per cent of sulphur other than that present as barytes.

as to show the effect upon the analysis of the two commonly used sulphates, barytes and sublimed lead, and the vulcanization was controlled so that one of the samples should have a rather large free sulphur content. These two samples have practically the same composition as many that are frequently met with in our routine work and may therefore be considered as representative of such materials.

V. METHODS COMPARED

Direct solution methods:

1. Spence and Young, concentrated HNO_3, fuming HNO_3 and electrolysis.
2. Deussen, concentrated HNO_3 and extraction with Na_2CO_3.

Direct fusion methods:

3. Alexander, Na_2O_2.
4. Joint Rubber Insulation Committee, Na_2O_2 and KNO_3.
5. Kaye and Sharp, ZnO and KNO_3.

Solution and fusion methods:

6. Frank and Marckwald, fuming HNO_3, fusion with Na_2CO_3 and KNO_3.
7. Waters and Tuttle, concentrated HNO_3 and Br, fusion with Na_2CO_3 and KNO_3.

Special method:

8. Acetone extraction, and separate determination of free and residual sulphur.

The methods as originally described by the various investigators were followed as closely as possible. Whenever it was considered advisable to depart from the original method the reasons therefor are given. Unless otherwise stated, 0.500 gram was taken for each determination. The "fusion mixture" used was composed of equal parts of sodium carbonate and potassium nitrate. Fusions were made with the gasoline gas generator described by Waters.[15] The barium sulphate precipitates were allowed to stand over night before filtering, and were ignited and weighed in porcelain crucibles. Insoluble residues were examined for sulphur, the amounts of which, if present in appreciable quantities, are given. The reagents used were tested and found

[15] J. Ind. & Eng. Chem., 5, p. 853; 1913.

to be practically free from sulphur, so that no corrections are necessary on their account. Methods 4, 6, 7, and 8 are intended to determine the total sulphur, while 1, 2, 3, and 5 are intended for the determination of sulphur other than that present as insoluble sulphates.

1. SPENCE AND YOUNG.—The rubber was treated with 5 cc of concentrated nitric acid, and heated gently. When the first reaction was over, about 50 cc (exact amount was not specified by the authors) of fuming nitric acid was added and the solution electrolyzed. As a source of current an 8-volt storage battery was used. This was connected directly to the platinum electrodes. The resistance of the electrolytic cell was such that the current was usually between 2 and 3 amperes, though at times it was as low as 1 ampere. After two or three hours, the current was discontinued, the electrodes removed, 1 gram of potassium nitrate [16] was added, and the solution evaporated to dryness. The nitric acid was completely removed with hydrochloric acid by several evaporations. A few drops of hydrochloric acid were added, the residue was treated with hot water, and filtered. The sulphur in the filtrate was precipitated as usual. The insoluble matter filtered off above was fused with 5 grams of fusion mixture, extracted with hot water, filtered, and after acidification the sulphur in the filtrate was precipitated as usual.

2. DEUSSEN.—The Deussen method was not followed exactly as given by the author. The rubber was treated in a porcelain crucible with concentrated nitric acid and covered. After heating for a short time, the cover was removed and the solution evaporated to dryness. The residue was treated with sodium carbonate and water, and after heating the solution was filtered. Up to this point the original method was followed exactly. Deussen reduces the sodium sulphate to sulphide and determines the latter colorimetrically. In order to avoid any error introduced by this procedure and to obtain a better comparison with the other methods, we added potassium nitrate to the filtrate, evaporated to dryness, and fused. The sulphur in the cooled melt was determined as

[16] Spence and Young add 1 gram of sodium carbonate, but inasmuch as this on solution is changed to sodium nitrate we used potassium nitrate, which serves the same purpose and obviates the spattering caused by the addition of a carbonate to the hot concentrated acid.

under the Waters and Tuttle method. The insoluble residue from the sodium carbonate filtration was fused with 5 grams of fusion mixture and the sulphur determined as usual.

3. ALEXANDER.—The Alexander method, as given in "Allen's Commercial Organic Analysis," is said to be rapid and reliable. The rubber is intimately mixed with 16 grams of sodium peroxide in an iron crucible provided with a lid through which a small hole has been bored. The combustion is started by introducing through this hole a red-hot iron wire. No further heating is required. When the mass is cool it is dissolved in water, the crucible, lid, and wire are removed, the solution is acidified with hydrochloric acid and boiled, filtered if necessary, and the sulphate precipitated by means of barium chloride.

4. JOINT RUBBER INSULATION COMMITTEE.—The rubber was fused with 4 grams of sodium peroxide and 6 grams of potassium carbonate. The cooled melt was extracted with hot water to which some bromine water had been added. The solution was filtered, acidified with hydrochloric acid, and evaporated to dryness to dehydrate silica. About 400 cc of water was added, the solution made slightly acid with hydrochloric acid, filtered, and the sulphur in the filtrate determined as usual.

5. KAYE AND SHARP.—The rubber was mixed with 4 grams of zinc oxide and 2 grams of potassium nitrate, placed in a crucible (both iron and porcelain were used), and covered with a layer of zinc oxide about 1 cm deep. This was carefully heated, at first with a low and afterward with a full Bunsen flame. The crucible and contents were placed in a beaker, covered with water and heated, the solution was acidified with hydrochloric acid and filtered. The sulphur in the filtrate was determined as usual.

The insoluble residue filtered off from the hydrochloric solution was fused with 5 grams of fusion mixture and the sulphur determined as under the insoluble matter in the Spence and Young method.

6. FRANK AND MARCKWALD.—The rubber was treated with about 20 to 25 cc of fuming nitric acid in a porcelain crucible, the vessel covered with a watch glass and allowed to stand overnight. The solution was evaporated to dryness, the residue fused with 5 grams of fusion mixture, extracted with hot water and

filtered. The filtrate was acidified with hydrochloric acid and the sulphur precipitated as usual.

7. WATERS AND TUTTLE.—The rubber was treated in a porcelain crucible with 25 cc of concentrated nitric acid saturated with bromine, the vessel covered with a watch glass, and allowed to stand one hour. It was heated on a steam bath for one hour and then the cover was removed and the solution evaporated to dryness. The residue was fused with 5 grams of fusion mixture, extracted with hot water, filtered, the filtrate acidified with hydrochloric acid, and the sulphur precipitated as usual.

8. EXTRACTION WITH ACETONE.—Some determinations were made by extracting 2 grams of rubber with freshly distilled acetone for eight hours. The acetone solution was evaporated to dryness, distilled water and bromine added, the solution heated until colorless, filtered, and the sulphur in the filtrate determined as usual. The insoluble residue was examined for sulphur by fusing with 5 grams of fusion mixture. The amount of sulphur thus found was scarcely ever more than a few tenths of a milligram.

The extracted rubber was dried at about 60° C and the sulphur determined according to the method of Waters and Tuttle. The sum of these various determinations should be the total sulphur.

VI. RESULTS OF TESTS

Method

Sample	1			2			4	5			6	7	8		
	Filtrate	Residue	Total	Filtrate	Residue	Total	Total	Filtrate	Residue	Total	Total	Total	Extracted	Residue	Total
A							4.90					4.87			
							4.94								
B				4.53	1.66	6.19	6.26	3.63	2.43	6.06	6.00	6.29	0.51	5.74	6.25
				4.84	1.41	6.25	6.31				6.18	6.30	.40	5.90	6.30
				3.84	2.74	6.58					6.26	6.33	.44	5.85	6.29
				3.89	2.65	6.54					6.28	6.35			
												6.42			
												6.42			
												6.43			
												6.44			

VI. RESULTS OF TESTS—Continued

Method—Continued

Sample	1			2			4	5			6	7	8		
	Filtrate	Residue	Total	Filtrate	Residue	Total	Total	Filtrate	Residue	Total	Total	Total	Extracted	Residue	Total
	.....	.....	.....	3.19	0.88	4.07	4.09	3.38	0.66	4.04	4.19	4.17	0.61	3.59	4.20
	.....	.....	.....	2.55	1.52	4.07	4.13	2.45	1.68	4.13	4.20	4.18	.63	3.60	4.23
C	.....	.....	.....	.....	.....	.....	4.19	3.32	.86	4.18	4.28	4.20	.60	3.64	4.24
	.....	.....	.....	.....	.....	.....	4.31	.....	.....	.....	.....	4.22	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.23	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.25	.....	.....	.....
	.....	.....	.....	.....	.....	.....	1.73	.....	.....	.....	.....	1.65	.....	.....	.....
	.....	.....	.....	.....	.....	.....	1.76	.....	.....	.....	.....	1.67	.....	.....	.....
D	.....	.....	.....	.....	.....	.....	1.78	.....	.....	.....	.....	1.70	.....	.....	.....
	.....	.....	.....	.....	.....	.....	1.80	.....	.....	.....	.....	1.73	.....	.....	.....
	.....	.....	.....	.....	.....	.....	1.81	.....	.....	.....	.....	1.75	.....	.....	.....
	.....	.....	.....	.....	.....	.....	1.83	.....	.....	.....	.....	1.78	.....	.....	.....
	4.91	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.95	.....	.....	.....
E	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.15	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.22	.....	.....	.....
	5.39	2.33	7.71	7.47	.47	7.94	7.78	6.89	.21	7.10	7.72	7.90	[a]3.59	4.22	7.81
	6.90	.88	7.78	7.74	.22	7.96	7.80	6.81	.38	7.19	7.78	7.96	[a]3.26	4.81	8.07
	6.42	1.36	7.78	.....	.....	.....	7.83	.....	.....	.....	7.80	7.96	4.02	4.06	8.08
	5.04	2.75	7.79	.....	.....	.....	8.01	.....	.....	.....	7.86	7.96	4.04	4.04	8.08
	4.67	3.17	7.84	.....	.....	.....	8.02	.....	.....	.....	7.88	8.00	.....	.....	.....
F	5.05	2.81	7.86	.....	.....	.....	.....	.....	.....	.....	.....	8.01	.....	.....	.....
	4.52	3.38	7.90	.....	.....	.....	.....	.....	.....	.....	.....	8.02	.....	.....	.....
	4.71	3.26	7.97	.....	.....	.....	.....	.....	.....	.....	.....	8.09	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.11	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.12	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.13	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.13	.....	.....	.....
	11.49	.35	11.84	5.52	4.04	9.56	10.98	9.89	.04	9.93	11.56	11.96	8.31	3.69	12.00
	11.45	.40	11.85	5.51	4.71	10.22	11.34	9.77	.57	10.34	11.64	12.00	8.14	3.88	12.02
	11.46	.39	11.85	8.33	2.81	11.14	12.04	9.80	.55	10.35	.....	12.04	8.06	3.97	12.03
	11.52	.34	11.86	7.96	3.43	11.39	12.10	10.74	.03	10.77	.....	12.08	.....	.....	.....
G	11.36	.53	11.89	.....	.....	.....	.....	10.42	.41	10.83	.....	12.16	.....	.....	.....
	11.57	.32	11.89	.....	.....	.....	.....	.....	.....	.....	.....	12.18	.....	.....	.....
	11.43	.47	11.90	.....	.....	.....	.....	.....	.....	.....	.....	12.19	.....	.....	.....
	11.56	.34	11.90	.....	.....	.....	.....	.....	.....	.....	.....	12.20	.....	.....	.....
	11.47	.45	11.92	.....	.....	.....	.....	.....	.....	.....	.....	12.23	.....	.....	.....
	11.44	.48	11.92	.....	.....	.....	.....	.....	.....	.....	.....	12.29	.....	.....	.....
	.....	.....	.....	15.77	4.94	20.71	20.52	15.68	5.20	20.88	20.71	21.09	9.60	11.52	21.12
	.....	.....	.....	15.69	5.16	20.85	20.68	.....	.....	.....	.....	21.16	.....	.....	.....
	.....	.....	.....	.....	.....	.....	20.74	.....	.....	.....	.....	21.20	.....	.....	.....
H	.....	.....	.....	.....	.....	.....	20.83	.....	.....	.....	.....	21.30	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	21.32	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	21.36	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	21.40	.....	.....	.....

[a] These two samples were not completely extracted.

VII. DISCUSSION OF RESULTS

Although the method of Waters and Tuttle is No. 7, it has been considered advisable to discuss it first, since it is the most reliable and accurate method we have found for the determination of total sulphur. The reaction proceeds slowly without any very great evolution of heat so that there is little or no chance of losing free sulphur. Even when the free sulphur is very high the method is adequate to determine it with accuracy. A large number of determinations were made, and the results are concordant and agree with the calculated results in samples of known composition.

The Waters and Tuttle method has been in use at the Bureau of Standards for a number of years and during that time has frequently been used in determining the total sulphur in samples of known composition. The results have invariably been satisfactory even when obtained by comparatively inexperienced analysts.

The methods which have been compared in the course of this investigation may be divided into two classes, viz, those for the determination of the total sulphur and those for the determination of sulphur other than that present in the insoluble sulphates. They may be further classified, according to the method of attack employed, as follows: Direct solution, direct fusion, and solution and fusion methods.

The methods which have for their object the determination of sulphur other than that present in the insoluble sulphates (Nos. 1, 2, 3, and 5) attempt to separate the insoluble sulphates by filtration. Spence and Young, Alexander, and Kaye and Sharp filter from an acid solution. The securing of correct results by this method is based upon the obviously incorrect assumption that the lead sulphate originally present would remain insoluble while that formed from the litharge would be completely dissolved. Deussen filters from an alkaline carbonate solution, but this procedure is open to the objection that lead sulphate will react with sodium carbonate solution with the formation of soluble sodium sulphate. It is apparent, therefore, that such methods cannot give reliable results since their basic principles are faulty.

Considering the methods as classified according to the mode of attack, we find that the direct solution methods (Nos. 1 and 2)

employ concentrated nitric acid. The use of this reagent in the determination of the total sulphur in rubber was first suggested by Henriques, and many investigators have shown that its use gives low results, probably on account of the loss of free sulphur. Even when the sulphur which is remaining in the insoluble residue is included with that in the filtrate, the sum does not equal the calculated value.

The direct fusion methods (Nos. 3, 4, and 5) give results which are satisfactory only when the free sulphur content is relatively low. In view of the results obtained by the other fusion methods it was not considered necessary to make any determinations by the Alexander method. The reaction between rubber and sodium peroxide often proceeds with explosive violence, particularly so when, as in this method, the sodium peroxide is not diluted with some less active flux. The more important points have been demonstrated by the results on the other methods, namely, first, that the direct fusion may give low results, and second, that the filtering of the solution of the melt after the addition of acid gives results which have no relation to the sulphur it is desired to determine.

Although the reaction during the fusion in the Kaye and Sharp method is not attended by any explosion, the results show that it is open to all the other objections which have been made above, hence it can not be relied upon to give results which have any significance.

The results obtained by the method of the Joint Rubber Insulation Committee (No. 4) are accurate when the free sulphur is low, as it is in insulation compounds, so that it may be relied upon to do all that this committee has claimed for it. This has been also substantiated by the work of the analytical committee of the Rubber Section of the American Chemical Society.[17] Whenever the free-sulphur content is high our results indicate that this method has the same serious defect as the other direct fusion methods.

The methods which require both solution and fusion yield the most satisfactory results. One of these (the Waters and Tuttle method) has already been referred to. The Frank and Marckwald

[17] J. Ind. and Eng. Chem., 6, pp. 514–518; 1914.

method is at times very satisfactory, but unfortunately it does not seem reliable with large amounts of free sulphur. The reaction between the rubber and the fuming nitric acid is at times very violent, and considerable heat is evolved. In fact, in several cases, by adding only 1 or 2 cc of the acid, the heat was so great as to cause the rubber to take fire. It seems probable that this heating is responsible for the loss of sulphur and the consequent low results.

In view of the fact that the free sulphur can be determined by several methods (one of which has already been described) with considerable accuracy in the acetone extract, and since this determination is usually made in analyses of vulcanized rubber goods, it is possible, and in some cases may be convenient, to determine the total sulphur by adding to the result for free sulphur the amount found in the residue after acetone extraction. Such a method would have the advantage of first removing the free sulphur, which has been found to be one of the most disturbing factors in many of the methods for the determination of total sulphur. Our experience indicates that accurate results can be obtained by this method.

We have determined the sulphur remaining in the rubber after the acetone extraction by the Waters and Tuttle method. It is more than possible that other methods will be equally efficient.

VIII. OUTLINE OF THE METHOD ADOPTED BY THE BUREAU OF STANDARDS

As the result of this and other investigations and the experience of the Bureau of Standards, extending over some years, we believe that the Waters and Tuttle method is the most reliable and it has been adopted for use in the routine work there. The determination is made as follows:

Half a gram of rubber is placed in a porcelain crucible of about 100 cc capacity, 20 to 25 cc of concentrated nitric acid which has been saturated with bromine is added, the crucible covered and allowed to stand for one hour. It is then heated gently for one hour, after which the cover is removed, rinsed with a little distilled water, and the solution is evaporated to dryness.

Five grams of fusion mixture (1–1 potassium nitrate and sodium carbonate) and 3 or 4 cc of distilled water are added, the mixture

is digested for a few moments on the steam bath and then spread halfway up the side of the crucible to facilitate drying. The drying is done either on a steam bath or electric hot plate, in the latter case care being taken to avoid spattering, caused by possible overheating. When dry the mixture is fused over a sulphur-free flame until all the organic matter has been destroyed and the melt is quite soft. The crucible and contents are cooled, placed in a 600 cc beaker, covered with distilled water, and heated on the steam bath for three or four hours. The solution is then filtered and the insoluble matter washed thoroughly. The combined filtrate and washings should amount to about 500 cc. About 7 or 8 cc of concentrated hydrochloric acid is added, the beaker covered, and the solution heated almost to boiling. The solution is now tested and if necessary made slightly acid toward Congo paper; if the directions have been followed exactly, there should be a slight excess of acid present. Ten cubic centimeters of 10 per cent barium chloride solution is added, and the solution is allowed to stand overnight. The precipitated barium sulphate is filtered off, and ignited over a small Bunsen flame, care being taken to see that the filter paper does not inflame. The barium sulphate is calculated to sulphur by means of the factor 0.1374.

IX. SUMMARY

It is shown that the methods which have been proposed for the determination of the total sulphur, other than that present as insoluble metallic sulphates, are not satisfactory.

It is shown that loss of sulphur is likely to occur in the direct fusion methods, and this loss is apt to increase with increasing free-sulphur content.

The method of Waters and Tuttle is recommended for the determination of total sulphur. This method is accurate and comparatively rapid, and has given satisfactory results in the hands of a number of analysts over a rather extended period of time.

A new suggestion is offered—namely, to determine separately the free sulphur and the sulphur remaining after the acetone extraction, reporting the sum of the two quantities as the total sulphur. This procedure eliminates the troublesome effect of the free sulphur upon the determination of the total sulphur.

The authors wish to express their appreciation of the many suggestions made by Dr. C. E. Waters, of this Bureau, and of the assistance given by the Voorhees Rubber Manufacturing Co., of Jersey City, N. J., in permitting us to make up some compounds of known composition in their factory.

WASHINGTON, December 1, 1914.

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

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VALUE OF THE HIGH-PRESSURE STEAM TEST OF PORTLAND CEMENTS

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I. INTRODUCTION

Unsoundness of a Portland cement, which is evidenced with age by a lack of cohesion and strength, may not be apparent for weeks or months after the cement is hydrated. This fact has created a demand for an accelerated test of soundness, in answer to which a large number of such tests have been proposed. All accelerated tests are designed to hasten the action of any expansive constituents of the cement, producing thereby evidence of unsoundness in a few hours or days.

High-pressure steam as a means of determining soundness apparently was first advocated in 1880 by Dr. Michaelas, who procured a German patent [1] on what he termed a boiling test

[1] Tonindustrie Zeitung, 1893, p. 8.

at higher temperatures in which the cement soundness test pieces were subjected in a steam-tight vessel to steam at 140° C to 180° C.

Dr. Erdmenger also advocated this test, and in 1881[2] published a description of his method of testing soundness of cement by means of high-pressure steam. He believed originally that it was the magnesia which caused unsoundness, and that this test detected the presence of magnesia in dangerous quantities. Later, however, he modified this opinion, as he found some cements which contained very little magnesia were unsound when exposed to high-pressure steam, while some cements containing a relatively large percentage of magnesia were found to be sound. For several years thereafter Dr. Erdmenger advocated the use of his high-pressure steam test in which he employed saturated steam at from 3 to 40 atmospheres pressure, and used pats, briquettes, and expansion bars for test pieces at various times.

It is the general opinion that the primary cause of unsoundness in Portland cement is attributable to the presence of free or loosely combined lime. Recent work by Phillips and Klein[3] in confirmation of this opinion reveals additional facts concerning the action of free lime in cement. Their conclusions may be summarized as follows:

> Free lime is generally noted in small amounts in well-burned, higher limed cements and in underburned, lower limed cements. On hydration, free lime, according to its fineness, hydrates as crystalline or amorphous calcium hydroxide. The disruption in cements in accelerated tests is due to the formation of the crystalline calcium hydroxide. Calcium hydroxide crystals are found in cement hydrated under normal conditions, but are not as large in size as those found in cement subjected to high-pressure steam.

Since there is no chemical means by which the percentage of free lime in cement can be determined and the identification of this constituent by optical means is difficult and limited, investigators have endeavored to find an economical physical test that would detect the presence of free lime in its dangerous form where it is liable to cause disintegration, cracking, and weakening of the cement.

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[2] Tonindustrie Zeitung, 1881, Nos. 24, 25, 26, and 27.
[3] Technologic Paper No. 42, Bureau of Standards.

To effect the quick expansion of the free lime or other expansive constituents, various experimenters have employed heat and water at various temperatures, steam at atmospheric pressure, and steam at pressures from 3 to 40 atmospheres. Accelerated tests may also be divided into qualitative and quantitative tests. In qualitative tests the unsoundness of the cement is exhibited by the development of cracks, the warping of test pieces, or their disintegration. In quantitative tests the amount of expansion of the cement or the effect on the strength of the cement is taken as the measure of the unsoundness.

In 1912 Force [4] recommended the use of a high-pressure steam test and in 1913 issued a specification which prescribed the following:

SOUNDNESS—FORCE AUTOCLAVE TEST

Three neat briquettes to be made up in the usual manner and allowed to remain in the damp closet for 24 hours. At the expiration of that time the briquettes are to be removed from the molds and placed in the autoclave, sufficient water being added to partly or wholly cover the briquettes. The autoclave is then closed, the burners being of sufficient size to raise the pressure to 295 pounds in not more than one hour. The pressure of 295 pounds shall be maintained for one hour longer, or a total time of two hours. The pressure is then to be gradually released, the briquettes taken out and placed in the moist closet, where they shall be allowed to remain for one hour. At the end of that time they are to be broken in the standard cement testing machine in the usual manner. The average tensile strength of the three briquettes taken from the autoclave must show a tensile strength of not less than 500 pounds per square inch. They must also show an increase of not less than 25 per cent over the average tensile strength of three briquettes broken at the end of 24 hours. A bar of neat cement, 6 inches long by 1 inch square, shall be made up at the same time the briquettes are made. This expansion bar to remain in the moist closet for 24 hours and to be removed along with the briquettes and tested with the briquettes in the autoclave, as indicated above. After one hour in the moist closet, this expansion bar shall not show an expansion greater than one-half of 1 per cent.

Several railroads and other corporations adopted this test into their specifications, which brought about considerable controversy between its advocates and the cement manufacturers. Many of the cement manufacturers refused to furnish cement upon a specification which included this test, believing the test to be an abnormal one not in any way measuring the relative soundness or cementing value of Portland cement as used normally in concrete. It was also suggested that this test be in-

[4] Engineering News, Jan. 13, 1912.

cluded in the United States Government Specification for Portland Cement.

The work reported in this paper was limited to a physical investigation of the use of high-pressure steam as a means of determining the soundness of Portland cement both as a qualitative and quantitative test. In a number of instances the auxiliary tests are not as complete as might be desired, but they are of interest and therefore the results are included.

It is desired to thank the following cement companies for furnishing some of the cements used in these tests and also for their active interest in the work: Alpha Portland Cement Co., Alpha, N. J.; Atlas Portland Cement Co., Northampton, Pa.; Dexter Portland Cement Co., Nazareth, Pa.; Edison Portland Cement Co., New Village, N. J.; Lehigh Portland Cement Co., Ormrod, Pa.; and Universal Portland Cement Co., Universal, Pa.

Acknowledgment is also made to the Association of American Portland Cement Manufacturers for their cooperation in obtaining the samples, the chemical division of the Bureau of Standards for the chemical analyses of cements, and to G. M. Williams for his assistance in conducting the tests.

II. SCOPE OF INVESTIGATION

The investigation reported in this paper was made to establish, if possible, a relationship between the behavior of Portland cements in high-pressure steam and their physical properties under normal conditions of use and exposure, and to determine what value, if any, the high-pressure steam test has as a means of detecting unsoundness which might cause a weakening or disintegration of the cement or concrete.

III. PROPERTIES OF MATERIALS USED IN TESTS

1. CHEMICAL

The complete chemical analyses of the cements used in this investigation are given in Table 1.

2. PHYSICAL

The physical properties of the cements are given in Table 2, and the physical properties of the aggregates used in the concrete will be found in Table 3.

TABLE 1

Chemical analyses of cements

Brand of cement	Lab. No.	Silica (SiO_2)	Iron (Fe_2O_3)	Alumina (Al_2O_3)	Lime (CaO)	Magnesia (MgO)	Sulphuric anhydride (SO_3)	Loss on ignition	Insoluble residue
A[1]	345–13	20.94	1.95	7.01	63.12	3.52	1 50	2.15	0.13
A[2]	406–13	21.46	2.10	6.74	62.10	3.46	1.52	1.39	.12
B[1]	948–12	21.24	2.25	7.67	61.60	3.00	1.84	1.42	.73
B[2]	949–12	20.48	2.30	7.70	62.10	2.85	1.78	1.96	.68
B[3]	303–12	20.79	2.40	7.64	62.42	2.98	1.73	1.02	.32
C[1]	1171–13	20.52	2.30	7.00	63.00	3.04	1.66	2.01	.35
C[2]	243–13	21.12	2.10	7.36	62.20	3.22	1.61	1.33	.67
	243a–13	20.88	2.45	6.81	62.62	3.24	1.66	2.31	.41
C[3]	397–13	21.54	2.25	7.19	61.62	3.18	1.64	1.22	.73
	398–13	21.50	2.45	7.09	61.72	3.11	1.64	1.13	.73
C[4]	1209–12	20.96	2.30	7.20	61.90	3.13	1.68	2.50	.45
D[1]	378–13	21.66	2.60	5.84	63.32	2.63	1.38	1.40	.60
	379–13	20.20	2.80	7.12	63.80	2.70	1.51	1.78	.42
D[2]	441–13	19.86	2.55	7.39	63.08	2.83	1.44	1.84	.18
D[3]	863–12	20.12	2.40	7.46	62.70	3.34	1.33	2.85	.79
D[4]	875–12	20.24	2.55	6.95	62.56	3.26	1.48	2.81	.18
D[5]	882–12	20.04	2.75	6.81	62.54	3.25	1.30	2.77	.19
E[1]	312–13	23.76	2.40	5.36	62.86	3.11	1.33	.68	.35
	313–13	23.66	2.15	5.51	62.80	3.21	1.29	1.54	.58
E[2]	421–13	22.14	2.50	6.56	62.96	3.00	1.43	2.03	.19
F[1]	459–13	20.32	2.80	5.56	62.76	4.42	1.63	2.22	.43
F[2]	178–92–12	21.96	2.15	5.67	64.50	1.82	1.19	2.21	.....
G[1]	1079–12	19.50	2.50	8.20	64.42	1.64	1.55	3.18	.22
G[2]	1080–12	19.56	2.50	8.10	63.72	1.70	1.45	2.95	.30
G[3]	1460–1–12	19.94	2.40	[a] 7.92	63.48	1.60	1.56	2.42	.87
G[4]	947–12	20.00	2.35	7.83	63.36	1.99	1.47	3.51	.73
G[5]	1081–12	21.64	2.50	6.42	63.94	1.80	1.63	1.72	.19
G[6]	175–6–13	19.54	3.50	[b] 7.92	62.94	1.54	1.55	2.02	.25
G[7]	442–13	19.64	3.07	[c] 8.31	62.90	1.35	1.55	2.48	.35
G[8]	435–12	20.04	2.85	[d] 8.49	63.06	1.91	1.56	1.67	.42
H[1]	532–12	19.42	7.35	5.71	63.36	1.06	1.25	1.18	.21
H[2]	901–12	19.80	7.73	5.35	63.22	1.11	1.29	1.46	.34
I[1]	1208–12	21.16	2.35	6.23	64.26	3.62	1.60	.94	.23
K	788–12	23.72	2.20	6.68	61.94	3.11	1.19	.62	.37
L	774–12	25.84	.30	6.46	61.76	1.34	1.75	1.74	.49
M	669–12	23.76	.30	7.42	62.76	1.13	1.38	3.04	.85

[a] Contains 0.47 per cent of Mn_3O_4.
[b] Contains 0.61 per cent of Mn_3O_4.
[c] Contains 0.64 per cent of Mn_3O_4.
[d] Contains 0.5 per cent of Mn_3O_4.

TABLE 2

Physical Properties and Tests of Cements

Brand of cement [a]	Lab. No.	Spec. grav.	Fineness, in per cent passing sieve—		Per cent water	Time of setting		Soundness [b] in standard steam 5 hours	Tensile strength [c] (lbs. per sq. in.)				Behavior in steam tests				Tensile strength (lbs. per sq. inch) Age 48 hours	
									7 days		28 days		Standard specifications		High-pressure steam			
			No. 100	No. 200		Initial	Final		Neat	Sand	Neat	Sand	Failed	Passed	Failed	Passed	After steam treatment at high pressure	Untreated
						h. m.	h. m.											
A[1]	345–13	3.17	94.2	76.2	21.5	3 15	7 25	O. K.	695	243	789	350	.....	3–18–13	3–22–13 5–13–13	5–30–13	(d)	.....
A[2]	406–13	3.15	94.8	75.6	21.0	2 55	6 45	O. K.	747	278	715	404	.....	4– 3–13	.....	3–31–13	483	258
B[1]	948–12	3.15	94.2	75.0	21.5	2 15	6 45	O. K.	538	189	638	306	.....	7–24–12	7–17–12 7–31–12	8– 2–13	(d)	.....
B[2]	949–12	*3.04 f 3.14	94.0	75.6	21.5	2 10	6 40	O. K.	614	212	736	337	.....	7–24–12	.....	6–10–12	452	282
B[3]	303–12	3.15	96.4	79.0	22.5	3 30	6 45	O. K.	647	320	713	364	.....	4– 8–12	4–30–12	8– 5–12	(g)	(g)
C[1]	1171–13	3.10	98.6	87.2	22.4	4 25	6 25	O. K.	812	296	773	376	.....	6–28–13	6–28–13	.....	.....	.....
C[2]	243–13	3.15	97.0	82.6	22.4	3 35	8 20	O. K.	731	356	724	414	.....	3–11–12	3–10–12	4– 5–12	(d)	.....
	243–13	3.18	95.6	77.6	22.4	3 30	7 35	O. K.	673	327	793	404	.....	3–21–12	3–22–12	4– 5–12	(d)	.....
C[3]	397–13	3.16	98.2	87.4	23.4	3 05	6 45	O. K.	846	349	631	429	.....	3–31–13	.....	3–31–13	530	316
	398–13	3.15	98.6	85.3	23.4	3 20	7 50	O. K.	778	386	677	455	.....	3–31–13	.....	3–31–13	588	253
C[4]	1209–12	3.10	97.2	82.4	22.0	3 20	5 50	O. K.	668	293	765	341	.....	9–12–12	.....	9–10–12	(g)	(g)
D[1]	379–13	3.15	96.6	77.6	25.5	3 20	7 40	(h)	435	200	509	264	3–25–12	3–27–13	3–25–13	5–23–13	(d)	.....
	379–13	3.14	96.4	78.8	25.5	3 25	7 55	(h)	553	230	554	307	3–25–12	3–27–13	5–12–13	5–23–13	(d)	.....
D[2]	441–13	3.13	97.2	82.2	27.0	4 30	8 40	O. K.	535	278	562	343	.....	4–15–13	.....	4–17–13	424	222
D[3]	863–12	3.12	94.4	76.6	24.0	3 05	8 05	O. K.	538	225	617	311	.....	7–24–12	7–26–12	.....	(g)	(g)
D[4]	875–12	3.11	93.6	76.0	24.0	2 25	6 40	O. K.	534	365	577	413	.....	7–24–12	7–26–12	.....	(g)	(g)
D[5]	882–12	3.09	94.4	77.6	24.0	2 20	6 35	O. K.	650	195	610	256	.....	7–24–12	7–25–12	.....	(g)	(g)

E[1]	312–13	3.22	92.4	72.5	20.0	3 40	7 55	(*i*)	684	210	851	293	3–16–13	4– 7–13	4– 7–13	12– 1–13	(*d*)	.....
		3.21	93.0	72.9	20.0	3 40	7 45	(*i*)	701	204	830	301	3–16–13	4– 7–13	7–12–13	12– 1–13	(*d*)	.....
E[2]	421–13	3.21	94.6	80.6	21.5	4 25	8 30	O. K.	557	287	690	380	.....	4– 8–13	.....	4–12–13	454	289
F[1]	459–13	3.17	94.4	83.3	20.8	5 15	9 00	(*j*)	811	217	827	304	4–25–13 4–29–13	5–12–13	5–12–13	5–23–13	(*d*)	.....
F[2]	178 192–12	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2– 8–12	.....	.....	4–23–12	(*g*)	(*g*)
G[1]	1079–13	3.11	97.6	86.0	22.0	2 15	5 15	O. K.	615	282	780	320	.....	7–29–13	7–30–12 8–20–12	9– 5–12	(*d*)	.....
G[2]	1080–12	3.08	97.2	79.2	22.0	2 15	5 10	O. K.	630	273	693	337	.....	8–10–12	*k* 7–24–12 8–20–12	.....	.....	.....
G[3]	1460–12	3.12	96.0	75.0	22.2	2 40	6 55	O. K.	532	235	701	321	.....	11– 4–12	*k*11– 4–12	.....	.....	.....
	1461–12	3.10	95.0	75.0	22.2	2 35	6 50	O. K.	603	224	682	344	.....	11– 4–12	*k*11– 4–12	.....	.....	.....
G[4]	947–12	*e* 3.05 *f* 3.12	96.2	76.2	22.0	1 50	6 35	O. K.	655	213	737	313	.....	7–13–12	.....	7–16–12	457	421
G[5]	1081–12	3.10	97.2	85.6	22.0	2 10	5 25	O. K.	682	264	834	382	.....	7–25–12	.....	7–26–12	513	389
G[6]	175–13	3.14	97.6	75.2	22.0	3 00	5 40	(*d*)	539	215	726	314	*k* 2–19–13	.....	.....	.....	.....	.....
G[7]	442–13	3.12	95.6	78.4	21.5	3 05	6 50	O. K.	669	265	708	335	.....	4–16–13	4–23–13	.....	(*g*)	(*g*)
G[8]	435–12	3.12	96.6	80.6	21.8	2 45	6 05	O. K.	(*g*)	(*g*)	(*g*)	(*g*)	.....	4–11–12	.....	4–27–12	(*g*)	(*g*)
H[1]	532–12	3.24	98.2	87.6	22.0	4 00	7 45	O. K.	836	332	793	337	.....	4–30–12	.....	5– 2–12	(*g*)	(*g*)
H[2]	901–12	3.22	98.4	85.6	22.0	3 30	8 15	O. K.	723	259	885	342	.....	7–24–12	.....	7–26–12	(*g*)	(*g*)
I	1208–12	3.14	98.2	85.2	22.0	3 10	5 55	O. K.	703	316	721	359	.....	9–12–12	.....	9–10–12	(*g*)	(*g*)
K	788–12	3.21	94.0	75.0	22.0	3 10	7 10	O. K.	595	216	683	307	.....	7–16–12	7–19–12	8– 5–12	(*g*)	(*g*)
L	774–12	3.15	98.6	86.4	22.0	0 35	2 00	O. K.	(*g*)	(*g*)	(*g*)	(*g*)	.....	7–12–12	.....	7–16–12	(*g*)	(*g*)
M	669–12	3.10	98.8	83.6	25.0	4 05	7 25	O. K.	(*g*)	(*g*)	(*g*)	(*g*)	.....	6– 7–12	.....	6–12–12	(*g*)	(*g*)

[a] All Portland cement except L, which is a white Portland, and M, which is sold as a nonstaining cement. Different brands are indicated by separate letters, while different samples are indicated by numeral subscripts.
[b] All cement sound in air and water when examined at end of 28 days.
[c] All tensile strength values are the average of 3 test pieces.
[d] Disintegrated.
[e] As received.
[f] After ignition.
[g] No briquettes made.
[h] Cracked and disintegrated.
[i] Warped and soft; warped and disintegrated.
[j] Complete disintegration.
[k] No further tests made.

TABLE 3

Physical Properties of Aggregates

Aggregate [a]	Weight per cubic foot (pounds)	Specific gravity	Per cent of voids computed	Mechanical analyses		
				Number of mesh	Opening in inches	Per cent passing
Potomac River sand	104	2.66	37.2	3	0.263	100.0
				4	.185	99.4
				6	.131	96.6
				8	.093	91.7
				10	.065	85.6
				14	.046	80.0
				20	.0328	71.0
				28	.0232	54.8
				35	.0164	37.9
				48	.0116	18.9
				65	.0082	9.3
				100	.0058	3.7
				150	.0041	1.9
				Screen (inches)		
Potomac River washed gravel	104	2.60	35.8	2.0	2.0	100.0
				1.5	1.5	96.5
				1.0	1.0	74.9
				.75	.75	59.8
				.50	.50	39.4
				.25	.25	13.4

[a] Both aggregates were composed chiefly of silicious material, were clean, and practically free from clay or loam.

IV. DESCRIPTION OF TESTS

The qualitative high-pressure steam test used throughout this paper consists of subjecting an ordinary soundness pat, which has been stored for 24 hours in a damp closet, to a steam pressure of 300 pounds per square inch for at least one hour, the total time in the high-pressure boiler being three hours. A cement was said to pass this test when it exhibited no cracking, warping, or disintegration on examination after the treatment. The quantitative high-pressure steam test consists of molding six briquettes of neat cement at normal consistency, storing these test pieces 24 hours in a damp closet, then subjecting three of them to an atmosphere of steam at 300 pounds pressure for at least one hour; total time in the high-pressure boiler being three hours. The briquettes (both treated and untreated) are then broken in

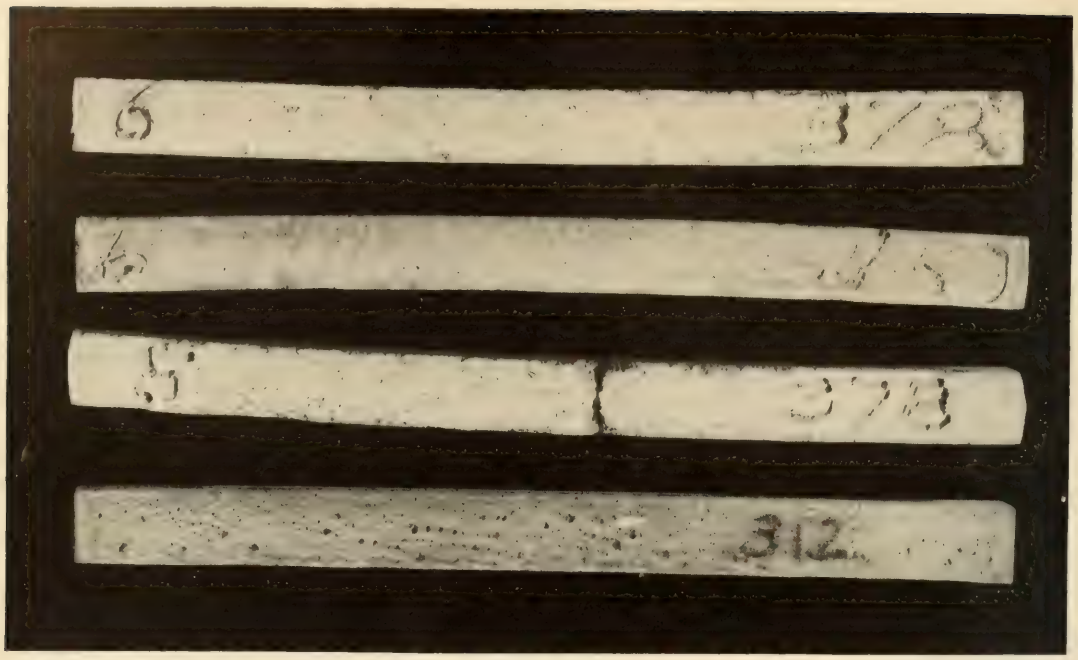

FIG. 1a.—*Neat cement prisms after storing for two years in air under cover*

All of the above prisms contained cement that passed the standard atmospheric steam test but failed in high-pressure steam at the time the prisms were molded. These prisms were merely stored in air and never treated in steam. Note the warping of all prisms and the partial disintegration of one prism marked 5–378, which broke in handling

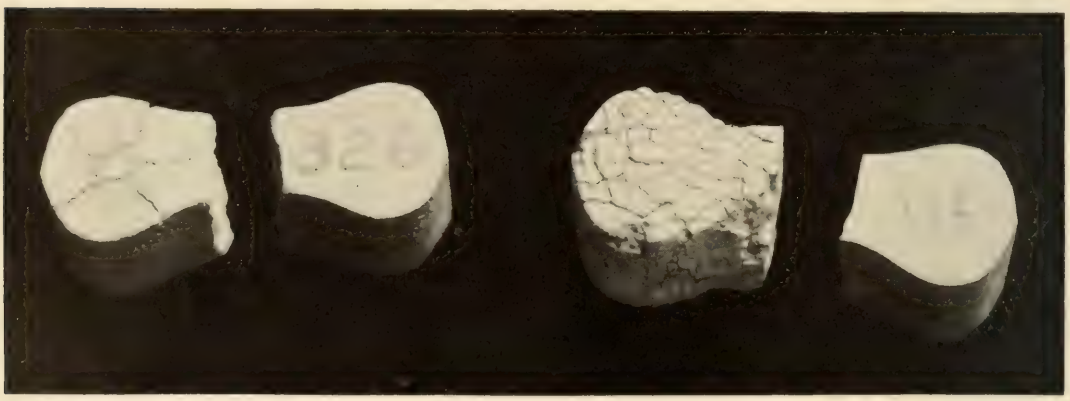

FIG. 1b.—*Effect of high-pressure steam on neat cement and mortar briquets*

All of the above half briquets contained cement that failed in the high-pressure steam test. Half briquets on the left are composed of 1:3 standard sand mortar. The one on the extreme left has been treated in steam at 180 pounds pressure for five hours, while the other half has not been treated. Half briquets on the right are composed of neat cement. The left one has been treated in steam at 180 pounds pressure for five hours, while the extreme right one has not been treated in steam

a shot-testing machine. A cement was said to pass this test when the treated briquettes exhibited greater strength than the untreated ones. Throughout this paper cements are classified into three types, respectively:

(1) A cement which fails to pass the standard atmospheric steam test.

(2) A cement which passes the atmospheric steam test but fails when treated in high-pressure steam.

(3) A cement which passes both atmospheric and high-pressure steam tests.

1. SOUNDNESS TESTS

Of a number of the routine samples of cement of various brands received in the Bureau laboratory, four soundness pats were made; one was stored in air at approximately 20° C (68° F), another placed in water at 20° C (68° F), the third treated in steam over boiling water at atmospheric pressure for five hours, while the fourth was subjected to 300 pounds steam pressure for at least one hour, total time in the high-pressure boiler being three hours. The results to date show, first, that all the type 1 cement that failed in the atmospheric steam test also finally failed as a neat cement pat stored in air, although they were sound at the 28-day period; and, second, that some of the cement classified as type 2 failed in air, while no cement of type 3, which passed the high-pressure steam test, failed in air. With one exception, all pats stored in water when last examined were sound. The cement which failed within two years showed some warping and was a type 2 cement. (See Fig. 1*a*.)

In Table 2 the results of the routine tests, including high-pressure steam tests of the cements used in the strength and linear change tests, are given.

In order to ascertain what proportion of the cements as at present manufactured were sound after exposure in high-pressure steam, all routine samples received for a period of about nine months were subjected to the qualitative high-pressure steam test, and the results are shown in Table 4 below. The qualitative high-pressure steam test was employed because the amount of cement which could be spared for these experiments was necessarily

small. The effect of high-pressure steam on neat cement which was unsound in high-pressure steam and one to three mortar of this cement is shown in Fig. 1*b*.

TABLE 4

Results of Tests of Portland Cement in High-Pressure Steam

Samples tested	Samples sound	Samples unsound	Brands sound	Brands unsound	Brands sound at one time, unsound at others
564.....	438	126	35	16	[a] 6
61 [b]	51	10	5	1	[a] 1

[a] These brands are included in other two columns.
[b] White Portland and natural so-called nonstaining cements.

In order to determine the effect of a small amount of free lime on the soundness of a cement, the following tests were made: Samples of chemically pure calcium carbonate, calcium sulphate, calcium nitrate, and limestone from the raw material taken at a cement mill were ignited in a vacuum furnace for a total time of from two to two and one-half hours, the maximum temperatures of 1400° C and 1700° C were maintained for at least one hour, and this calcined material added to a sound cement in two proportions, 0.5 and 4 per cent, respectively. The results are given below in Table 5. None of the compounds burned at either 1400° C (2552° F) or 1700° C (3092° F) when added to the cement to the amount of 0.5 per cent caused unsoundness even in high-pressure steam. It is observed that the limestone ignited at 1400° C and added to the amount of 4 per cent to a sound cement caused it to disintegrate, while the same cement, to which 4 per cent of the other calcium compounds ignited at the same temperature was added, was sound after exposure in both the atmospheric and high-pressure steam test.

TABLE 5

Results of Soundness Tests of Portland Cement to which Calcined Limestone, Calcium Carbonate, Sulphate, and Nitrate were added

Compound [a]	Temperature to which compound was heated	Per cent of ignited compound added to cement	Treatment of pat	Result of treatment
	°C[b]			
1	1400	0.5	In steam at atmospheric pressure, 5 hours.	All sound.
2	1400	0.5		
3	1400	0.5		
4	1400	0.5		
1	1400	0.5	In steam at 300 pounds, 1 hour; total time, 3 hours.	All sound.
2	1400	0.5		
3	1400	0.5		
4	1400	0.5		
1	1700	0.5	In steam at atmospheric pressure, 5 hours.	All sound.
2	1700	0.5		
3	1700	0.5		
4	1700	0.5		
1	1700	0.5	In steam at 300 pounds, 1 hour; total time, 3 hours.	All sound.
2	1700	0 5		
3	1700	0.5		
4	1700	0.5		
1	1400	4	In steam at atmospheric pressure, 5 hours.	Sound.
2	1400	4		Sound.
3	1400	4		Sound.
4	1400	4		(c)
1	1400	4	In steam at 300 pounds, 1 hour; total time, 3 hours.	Sound.
2	1400	4		Sound.
3	1400	4		Sound.
4	1400	4		(c)
1	1700	4	In steam at atmospheric pressure, 5 hours.	(c)
2	1700	2		Sound.
3	1700	4		(c)
4	1700	4		(c)
1	1700	4	In steam at 300 pounds, 1 hour; total time, 3 hours.	(c)
2	1700	2		Sound.
3	1700	4		(c)
4	1700	4		(c)

[a] Compound 1, calcium carbonate; compound 2, calcium sulphate; compound 3, calcium nitrate; compound 4, limestone from raw material taken at cement mill.

[b] This temperature was maintained in vacuum furnace for at least 1 hour; total time in furnace from 2 to 2½ hours.

[c] Completely disintegrated before treating in steam.

2. STRENGTH TESTS

A series of mortar strength tests were made, employing nine different samples of cement, comprising five different brands, three of these being of cements of type 1, failing to pass standard atmospheric steam test and the high-pressure steam test two of type 2, which passed in the atmospheric steam test and failed in the high-pressure steam test, and four of type 3, passing the high-pressure steam test and the atmospheric steam test. The mortar was composed of one part cement to three parts standard Ottawa sand, by weight, mixed at a consistency corresponding to the normal consistency of the cement used and molded by hand in brass molds. Both briquettes and 2-inch cubes were molded, and the test pieces were tested, or are to be tested, at various intervals up to 10 years. The results of these tests up to the present time are shown in Table 6 and diagrammatically in Figs. 2 and 3. All test pieces were stored in air except where noted.

A series of concrete strength tests were made to determine the cementing value of the three types of cements as normally used in concrete mixtures without exposure to steam. Eighteen samples of cement were employed, comprising seven different brands, four of these samples being of type 1, seven of type 2, and seven of type 3. The test pieces were concrete cylinders 8 inches in diameter by 16 inches high. The concrete was composed of one part cement, two parts Potomac River sand, and four parts washed Potomac River gravel, by volume. A medium consistency was employed containing about 9 per cent of water and the concrete was mixed in a one-half-yard cube mixer and molded by hand in steel molds. These cylinders, of which 45 were molded for each sample of cement, were tested, or are to be tested, at various intervals up to 10 years. All test pieces were kept in a damp place for 30 days, and then stored in air outdoors for the remaining time prior to testing. Three test pieces were tested at each test period, and the modulus of elasticity, together with the yield point, was determined on at least two of the cylinders of each set.

The results of the concrete strength tests to date are shown in Table 7 and diagrammatically in Fig. 4.

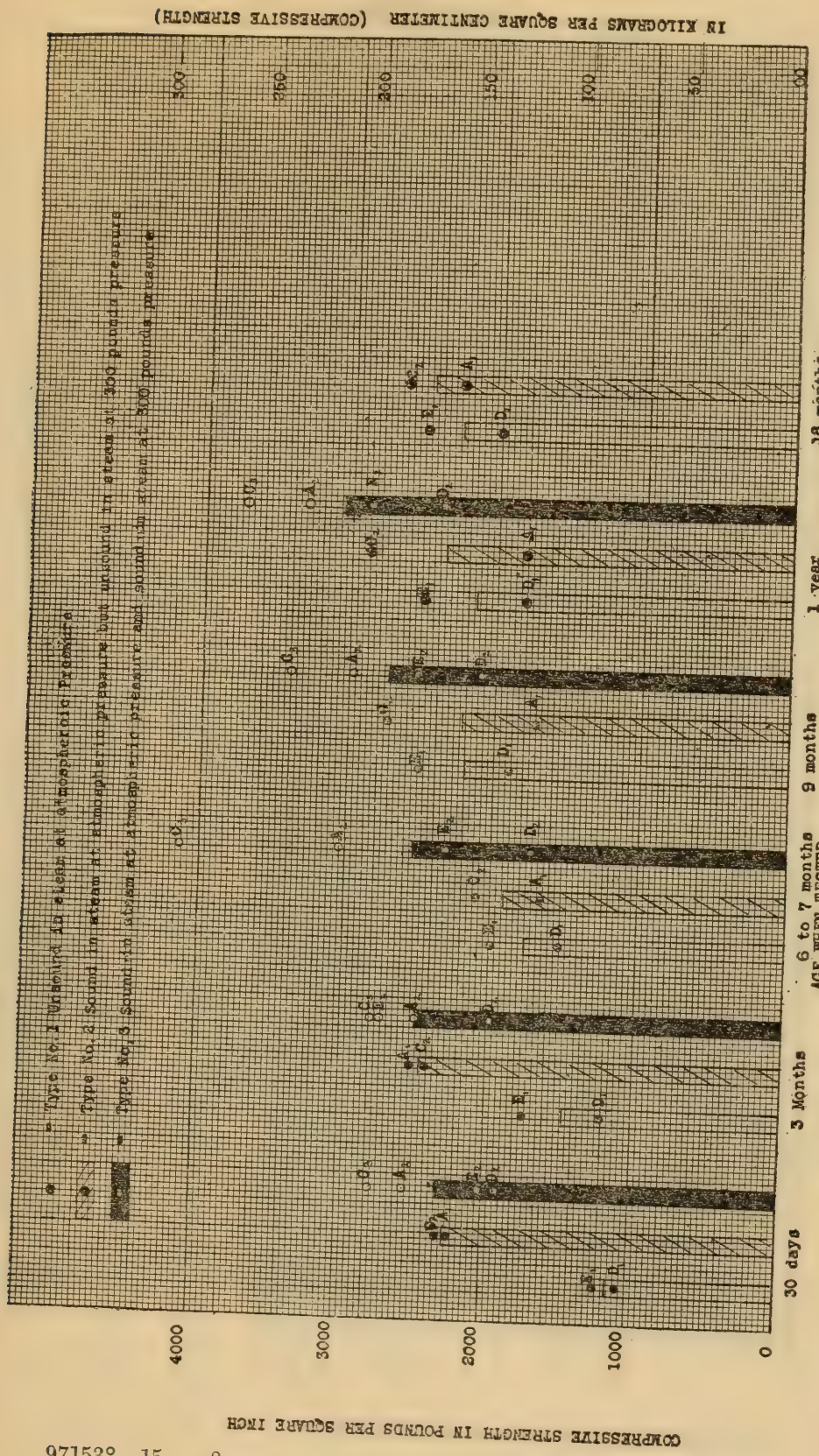

FIG. 2.—*Compressive strength of cement mortar made in connection with the investigation of the high-pressure steam test for Portland cement*

One part Portland cement to three parts standard Ottawa sand. Stored in air under cover at about 20° C. Each result is the average of tests of three 2-inch cubes.

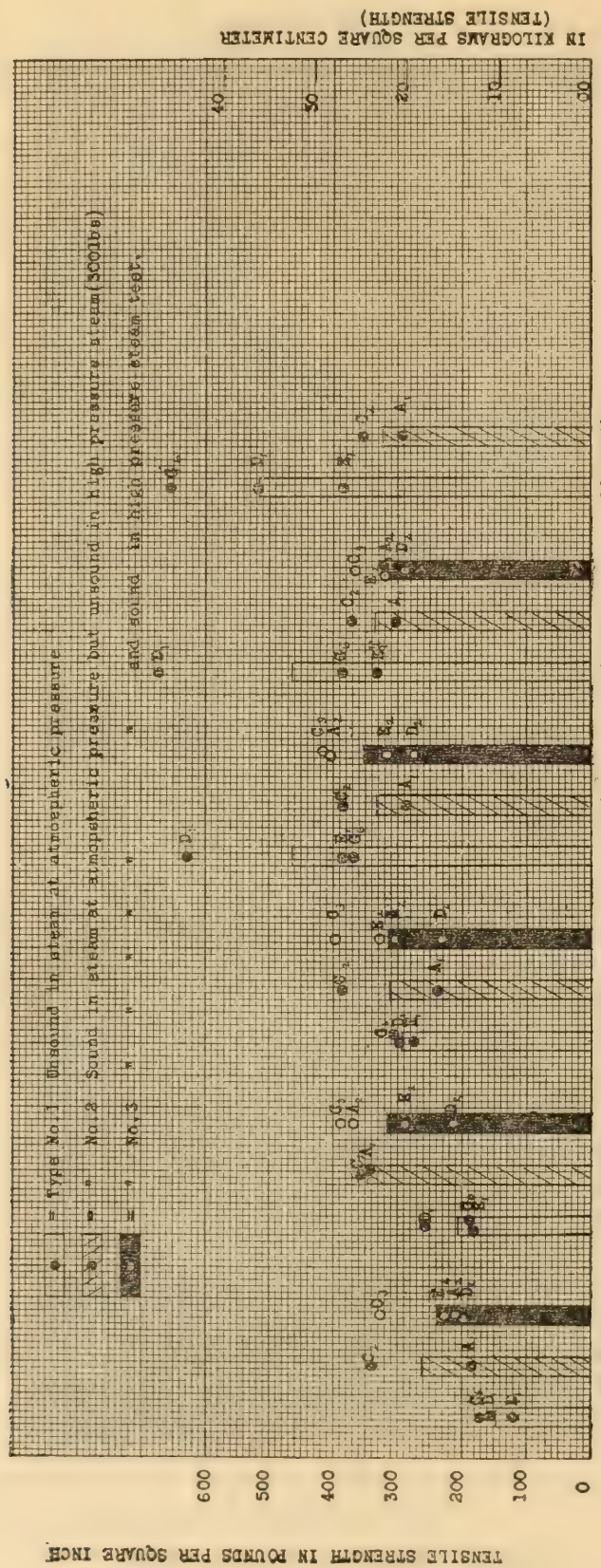

FIG. 3.—*Tensile strength of cement mortar made in connection with the investigation of the value of the high-pressure steam test for Portland cement.*

One part Portland cement to 3 parts standard Ottawa sand. Stored in air under cover at about 20° C. Each result is the average of tests of five standard briquettes.

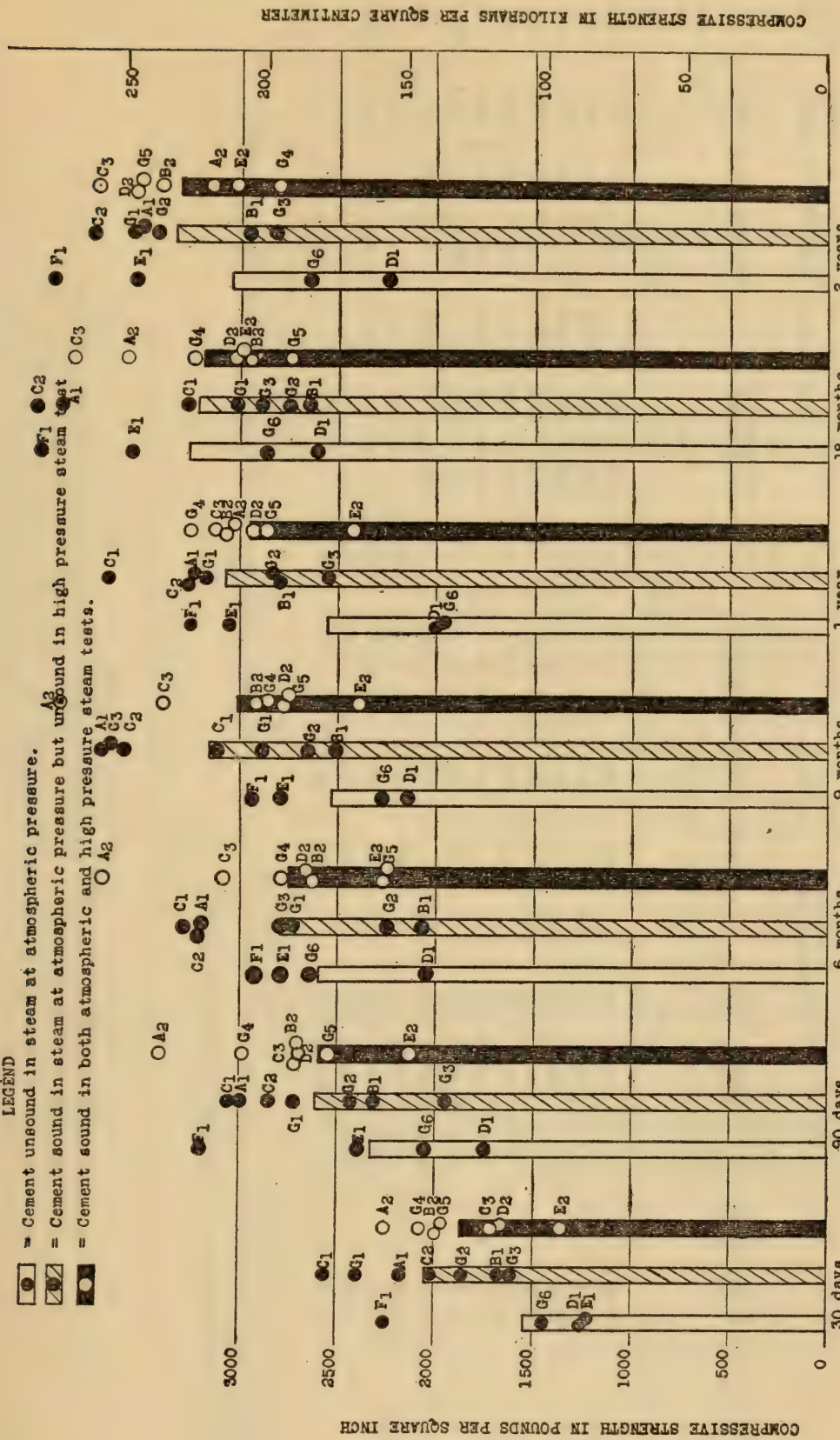
LEGEND
= Cement unsound in steam at atmospheric pressure.
= Cement sound in steam at atmospheric pressure but unsound in high pressure steam test
= Cement sound in both atmospheric and high pressure steam tests.
COMPRESSIVE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
COMPRESSIVE STRENGTH IN POUNDS PER SQUARE INCH
AGE WHEN TESTED
30 days
90 days
6 months
9 months
1 year
18 months
2 years

FIG. 4.—*Compressive strength of concrete cylinders made in connection with the investigation of the value of the high-pressure steam test for Portland cement*

Proportions: 1:2:4 by volume; 9 per cent water used; aggregates are Potomac River sand and washed gravel; stored in air outdoors. Each dot represents the average result of three tests of 8 by 16 inch cylinders. Different brands are designated by letter and separate shipments by subnumbers.

TABLE 6

Mortar Strength Tests Made in Connection with the Investigation of the Value of the High-Pressure Steam Test

[One part Portland cement, 3 parts standard Ottawa sand; stored in air except where noted]

Brand of cement	Lab. No.	Type of cement[a]	Tensile strength[b] (lbs. per sq. in.)									Compressive strength (lbs. per sq. in.)						
			Age in weeks when tested			Age in months when tested						Age in weeks when tested		Age in months when tested				
			1	4	13	6	7	9	12	18	24	4	13	6	7	9	12	18
A[1]	345–13	2	.....	186	341	.....	238	290	302	293	.....	2220	2508	.....	1655	1720	1805	2268
A[2]	406–13	3	.....	209	368	305	.....	406	317	.....	.....	2540	2481	3040	.....	2960	3300	.....
C[2]	243–13	2	.....	340	355	.....	386	383	371	354	.....	2290	2405	2102	.....	2735	2870	2640
C[3]	397–13	3	.....	325	387	398	.....	416	367	.....	.....	2775	2790	4140	.....	3400	3715	3440
D[1]	378–13	1	.....	156	256	.....	299	627	671	519	.....	1072	1210	.....	1532	1890	1800	2000
D[2]	441–13	3	.....	199	212	231	.....	274	290	.....	.....	1915	1970	1730	.....	2090	2380	.....
E[1]	312–13	1	.....	120	182	.....	276	386	333	381	.....	1220	1735	.....	1990	2510	2500	2490
E[2]	421–13	3	.....	227	289	329	.....	316	320	.....	.....	2020	2730	2320	.....	2530	2875	.....
G[5]	176–13	1	179	171	186	.....	305	369	387	655	817	.....	.....	.....	.....	.....	.....	.....
G[6]	176–13	1	[c] 216	[c] 294	[c] 308	.....	[c] 281	[c] 298	[c] 308	[c] 303	[c] 281	.....	.....	.....	.....	.....	.....	.....
G[6][d]	176–13	1	469	401	576	.....	543	607	548	665	670	.....	.....	.....	.....	.....	.....	.....
G[6][d]	176–13	1	[c] 648	[c] 658	[c] 726	.....	[c] 777	[c] 660	[c] 709	[c] 750	[c] 708	.....	.....	.....	.....	.....	.....	.....

[a] See p. 11.
[b] In the tensile-strength tests, each value is the average of tests of 5 briquettes; compressive-strength tests, each value is the average of three 2-inch cubes.
[c] Stored in water.
[d] In the tensile-strength tests neat-cement briquettes were used.

TABLE 7

Compressive Strength, in Pounds per Square Inch, of Concrete Cylinders Made in Connection with the Investigation of the Value of the High-Pressure Steam Test

[Concrete composed of 1 part Portland cement, 2 parts Potomac River sand, and 4 parts washed Potomac River gravel; percentage of water 9; stored in air outdoors; each result is the average of 3 test pieces.]

Brand of cement, etc.	Lab. No.	Type of cement [a]	Property determined	Age, in weeks, when tested (lbs. per sq. in.)		Age, in months, when tested (lbs. per sq. in.)				
				4	13	6	9	12	18	24
A[1]	345–13	2	Compressive strength	2178	2994	3197	3700	3237	3903	3512
			Modulus of elasticity	3 130 300	3 970 000	3 713 000	3 175 000	3 775 000	3 590 000	3 708 000
			Yield point	1275	1755	1680	2070	1920	2200	1930
A[2]	406–13	3	Compressive strength	2257	3400	3697	3910	3033	3573	3154
			Modulus of elasticity	3 150 000	3 862 000	3 903 000	3 960 000	3 333 000	4 150 000	3 810 000
			Yield point	1085	1750	2230	2035	1960	2070	1700
B[1]	948–12	2	Compressive strength	1680	2310	2075	2501	2790	2650	2960
			Modulus of elasticity	2 046 000	2 740 000	3 196 000	2 840 000	3 361 000	3 103 000	2 980 000
			Yield point	763	1287	900	1380	1325	1260	1450
B[2]	949–12	3	Compressive strength	1988	2690	2630	2909	3062	2953	3408
			Modulus of elasticity	2 459 000	3 350 000	3 220 000	3 265 000	3 030 000	3 397 000	3 260 000
			Yield point	697	1433	1350	1630	1615	1410	1760
C[1]	1171–13	2	Compressive strength	2560	3050	3205	3117	3663	3277	.....
			Modulus of elasticity	3 025 000	3 070 000	2 540 000	3 170 000	3 060 000	3 325 000	.....
			Yield point	1570	1650	1860	1660	2025	1750	.....
C[2]	243–13	2	Compressive strength	2017	2841	3283	3577	3258	4045	3749
			Modulus of elasticity	2 825 000	3 611 000	3 745 000	3 485 000	3 835 000	3 958 000	3 983 000
			Yield point	1110	1787	1675	2130	1800	1950	1640

[a] See p. 11.

TABLE 7—Continued

Brand of cement, etc.	Lab. No.	Type of cement	Property determined	Age, in weeks, when tested (lbs. per sq. in.)		Age, in months, when tested (lbs. per sq. in.)				
				4	13	6	9	12	18	24
C[3]	397–13	3	Compressive strength	1717	2713	3080	3383	3123	3853	3729
			Modulus of elasticity	3 015 000	3 091 000	3 450 000	2 910 000	3 091 000	3 517 000	3 688 000
			Yield point	790	1500	1825	2040	1750	2100	1800
D[1]	378–13	1	Compressive strength	1257	1753	2047	2145	2005	2610	2243
			Modulus of elasticity	2 380 000	3 053 000	3 660 000	3 020 000	3 280 000	3 275 000	4 245 000
			Yield point	490	1000	1030	1040	935	1225	983
D[2]	441–13	3	Compressive strength	1675	2700	2658	2778	2937	3027	3531
			Modulus of elasticity	2 930 000	4 120 000	4 185 000	3 691 000	3 510 000	4 165 000	4 080 000
			Yield point	855	1625	1490	1370	1840	1875	2090
E[1]	312–13	1	Compressive strength	1222	2309	2788	2793	3058	3547	3535
			Modulus of elasticity	3 100 000	3 170 000	3 110 000	2 842 500	3 750 000	3 888 000	4 037 000
			Yield point	580	1300	1445	1690	1750	1650	1727
E[2]	421–13	3	Compressive strength	1360	2135	2270	2395	2422	2983	3032
			Modulus of elasticity	2 390 000	3 285 000	3 745 000	3 050 000	3 306 000	4 140 000	3 940 000
			Yield point	660	1240	1240	1330	1250	1860	1510
F[1]	459–13	1	Compressive strength	2256	3197	2923	2940	3252	4017	3953
			Modulus of elasticity	2 960 000	2 935 000	3 105 000	2 940 000	3 175 000	4 040 000	4 215 000
			Yield point	845	1850	1410	1870	1865	3100	1695
G[1]	1079–12	2	Compressive strength	2390	2720	2735	2883	3167	3017	3541
			Modulus of elasticity	2 541 000	3 157 000	3 453 000	3 627 000	2 970 000	3 030 000	3 115 000
			Yield point	963	1390	1293	1490	1730	1675	1900
G[2]	1080–12	2	Compressive strength	1860	2430	2250	2656	2803	2757	3432
			Modulus of elasticity	2 603 000	2 696 000	3 450 000	3 250 000	3. 415 000	2 925 000	3 485 000
			Yield point	597	1183	860	1375	1450	1470	1780

G^3	1460–12	2	Compressive strength	1615	1950	2792	3657	2555	2888	2827
			Modulus of elasticity	2 500 000	2 920 000	4 020 000	3 875 000	3 136 000	3 340 000	3 140 000
			Yield point	783	1150	1470	1800	1520	1505	1900
G^4	947–12	3	Compressive strength	2074	2980	2690	2865	3250	3237	2807
			Modulus of elasticity	2 980 000	3 123 000	3 050 000	3 240 000	3 145 000	3 050 000	2 465 000
			Yield point	577	1450	1385	1500	1670	1890	1500
G^5	1081–12	3	Compressive strength	1972	2550	2250	2766	2870	2746	3517
			Modulus of elasticity	2 131 000	3 006 000	3 510 000	2 855 000	2 665 000	2 755 000	3 725 000
			Yield point	713	1240	1097	1245	1450	1500	1850
G^6	175–13	1	Compressive strength	1442	2050	2640	2277	1965	2865	2447
			Modulus of elasticity	1 962 000	3 315 000	2 810 000	3 070 000	2 910 000	3 077 000	3 257 000
			Yield point	650	1025	1215	1440	910	1630	970
Summary with reference to type of cement										
Type		1	Compressive strength	1544	2327	2599	2531	2556	3260	3045
			Modulus of elasticity	2 580 000	3 143 000	3 171 000	2 968 000	3 279 000	3 570 000	3 939 000
			Yield point	641	1294	1275	1510	1365	1901	1344
Type		2	Compressive strength	2043	2614	2791	3156	3067	3220	3337
			Modulus of elasticity	2 667 000	3 166 000	3 445 000	3 346 000	3 364 000	3 324 000	3 420 000
			Yield point	1009	1457	1391	1701	1681	1687	1767
Type		3	Compressive strength	1867	2596	2754	3001	2957	3196	3311
			Modulus of elasticity	2 722 000	3 405 000	3 580 000	3 281 000	3 154 000	3 596 000	3 567 000
			Yield point	768	1463	1517	1593	1648	1815	1744

A study of the effect of various steam pressures on cement passing the standard steam test is shown in Table 8. This table includes the results of tests of steam-treated mortar specimens two days old (just after removal from steam boiler), and similar results of tests when the steam-treated specimens are 28 days old. The results show that after the steam pressure has been raised to 100 pounds there is practically no increase in strength due to storing the treated test specimens for an additional 26 days in water before testing. The maximum tensile strength for this cement appears to have been attained with 140 pounds steam pressure.

An investigation reported in Technologic Paper No. 5,[5] which contains the results of tests of 8 by 16 inch mortar and concrete cylinders exposed to steam at pressures up to 80 pounds per square inch for various durations, showed that this treatment increases the compressive strength several hundred per cent, the maximum strength being obtained at the maximum steam pressure and duration.

[5] The Effect of High-Pressure Steam on the Crushing Strength of Portland Cement Mortar and Concrete; Technologic Paper No. 5, Bureau of Standards.

TABLE 8

Effect of Various Steam Pressures on Tensile and Compressive Strength of 1:3 Portland Cement Standard Ottawa Sand Mortar

Cement[a]	Steam pressure (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)		Compressive strength (lbs. per sq. in.)	
		48 hours	28 days	48 hours	28 days
A	10	118	261	.....	.....
A	20	117	218	1,915	2,591
A	40	115	190	1,176	2,262
A	60	151	215	1,750	2,385
A	80	195	260	1,890	2,178
A	100	294	315	3,397	2,867
A	100	381	366	.....	.....
A	100	[b] 514	425	.....	.....
A	120	385	358	2,485	2,353
A	140	410	411	2,965	2,537
A	160	363	355	2,912	2,327
A	180	362	286	3,198	3,050
A	180	[c] 369	[c] 256	3,416	3,079
A	180	[d] 398	[d] 272	.....	.....
B	200	245	288	.....	.....
B	275	[e] 218	193	.....	.....
B	225	[f] 211	219	.....	.....

[a] All subjected to steam at stated pressures for 5 hours unless otherwise noted. Both cements A and B passed the standard soundness test. All test pieces placed in boiler after 24 hours in damp room. Al values are the average of 3 test pieces.

[b] Age, 7 days. Under pressure at 100 pounds for 15 hours.

[c] Two periods of 5 hours each.

[d] Three periods of 5 hours each.

[e] Exposed to one period of 5 hours at 200 pounds pressure then one period of 5 hours at 275 pounds.

[f] Exposed to 5-hour periods each at 200 pounds, 275 pounds, and 225 pounds pressure.

3. LINEAR CHANGE TESTS

Tests were made on a large number of cement samples of various brands and comprising the different types of cement to determine the linear change occurring in these cements when stored in air, water, or treated in high-pressure steam. The test pieces employed were 1 by 1 by 13 inch prisms, and in most of the tests they were composed of neat cement gaged at normal consistency. For the first 24 hours after molding all test pieces were stored in a damp closet. They were then removed, and

by means of a mounted micrometer reading to thousandths of an inch the original reading was made. All the molds in which the test pieces were made were approximately 13 inches in length, and this was considered the original length by which all changes in length were divided to determine the per cent of linear change.

The results of the tests made on prisms stored in air and water are given in Table 9.

The effect on the length of the prisms of treating them in high-pressure steam is shown in Table 10. Fig. 5 shows one of these prisms of cement unsound in high-pressure steam before and after exposure to steam.

The effect on the length of these cement prisms of storing them in air and water is also shown in Fig. 6. While the results obtained with different cements overlap a good deal, it is evident that there is a tendency for the type 3 cement to show more contraction in air and less expansion in water than the type 2 cement. This would indicate that the type 2 cement contained a certain amount of expansive material, which in time tended to counteract the effect of contraction due to drying in air and added to the expansion caused by immersion in water. If this be definitely established, a type 3 cement would be less desirable than a type 2 cement in ordinary construction work exposed in the air.

Several tests were made to determine the linear change which occurred with cements to which sand or waterproofing compound are added. To one cement failing in the high-pressure steam test an equal part of standard Ottawa sand was added and a prism molded. This prism was then subjected to 180 pounds steam pressure for five hours and the linear expansion determined. A similar test prism containing one part cement to two parts standard sand was molded and treated in high-pressure steam. It was found that the linear expansion of the 1 : 1 mortar was 96 per cent of that of the neat cement, and the 1 : 2 was 69 per cent of that of the neat. All test specimens received the same steam treatment. To one cement 2 per cent of an integral antipathetic waterproofing compound, composed of stearic acid and lime, was added, and its effect on the linear change of test prisms stored in air and water was studied. The results show that the presence of the waterproofing compound had no effect on the linear change.

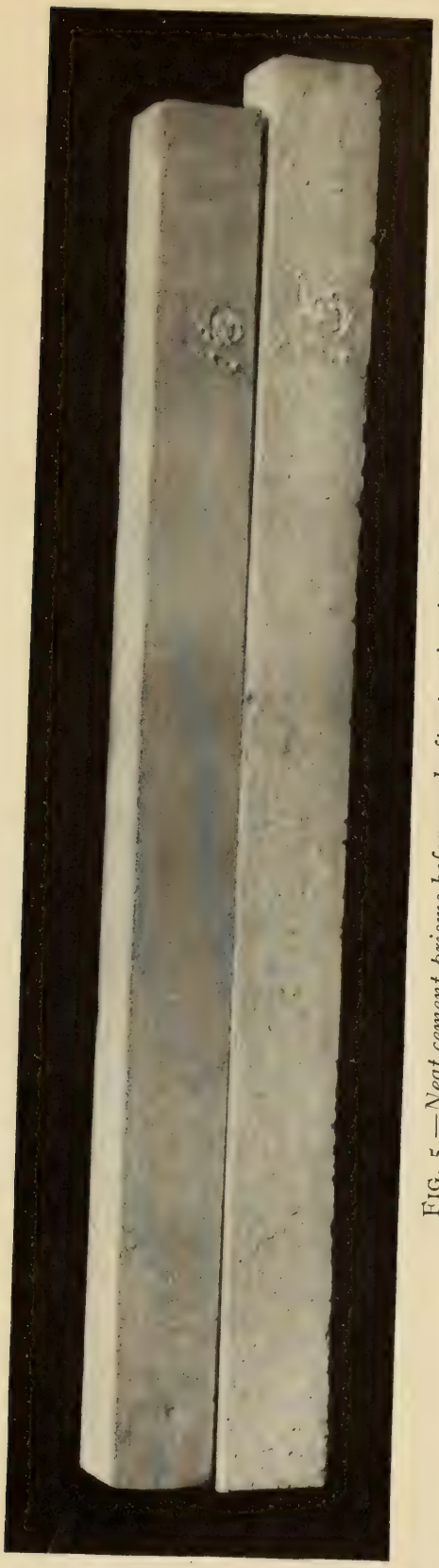

FIG. 5.—*Neat cement prisms before and after treating in high-pressure steam*

Both prisms contained cement that failed when exposed to high-pressure steam test. Prism No. 15 after treating in steam at 180 pounds pressure for five hours increased 4.7 per cent of original length. Prism No. 16 before treating in high-pressure steam

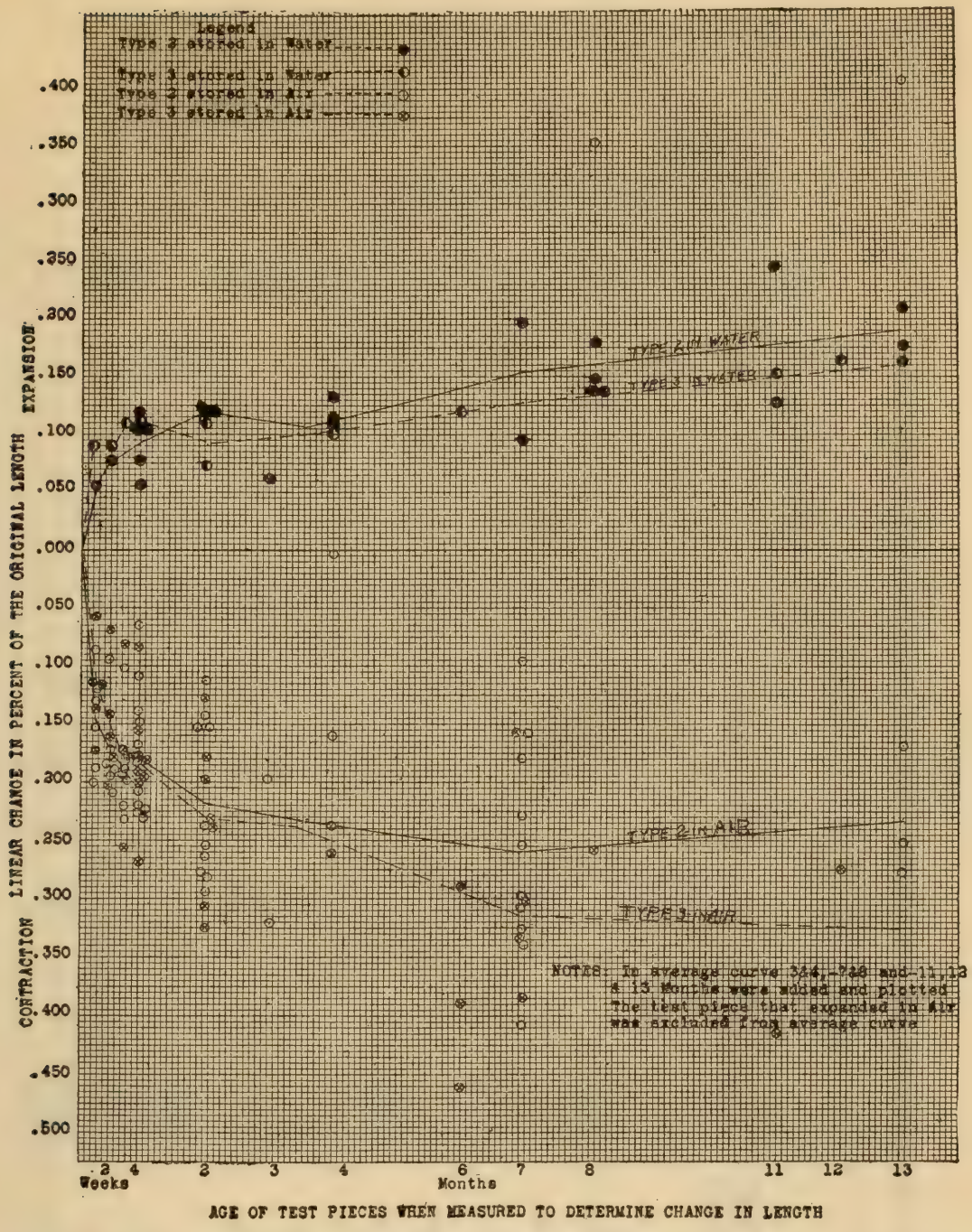

FIG. 6.—*Linear change of neat cement prisms stored in air and water made in connection with the investigation of the value of the high-pressure steam test for Portland cement*

Each dot represents the average results given in Table 9. Test pieces 1 by 1 by 13 inches neat cement prisms. Linear change in per cent of original length.

TABLE 9

Summary of Linear-Change Tests of Neat Cement Stored in Air and Water

[Test pieces 1 by 1 by 13 inch prisms]

Brand of cement [a]	Lab. No.	Type of cement [b]	Manner of storing	Test pieces, with average and range	Linear change in per cent of original length [c]												
					Age, in weeks, of test pieces				Age, in months, of test pieces								
					1	2	3	4	2	3	4	6	7	8	11	12	13
A[1]	345–13	2	Air	2 Average				0.182	0.237				0.254				[d] 0.277
				2 Range				.025	.009				.002				
B[1]	948–12	2	Air	6 Average	0.132	0.195	0.232	.228	.282	[e] 0.321			.408				
				6 Range	.019	.036	.035	.020	.025	.007			.010				
B[1]	948–12	3	Air	4 Average	.173	.204	.257	.269	[e] .306			[e] 0.461	[e] .385				
				4 Range	.062	.075	.041	.080	.007			.039	.022				
C[2]	243–13	3	Air	2 Average				.192	.177		0.238			0.257		0.275	
				2 Range				.034	.026		.021			.006		.010	
C[3]	397–13	3	Air	2 Average					.325			[d] .390			[d] 0.415		
				2 Range					.001								
D[4]	875–12	2	Air	1	.118	.191	1.97	.229	.294				.340				
D[3]	863–12	2	Air	2 Average	.200	.173	.190	.209	.254				.297				
				2 Range	.029	.012	.015	.020	.025				.037				
D[5]	882–12	2	Air	2 Average	.188	.186	.197	.220	.263				.309				
				2 Range	.026	.017	.017	.017	.014				.011				
D[1]	378–13	2	Air	2 Average				.149	.153		.003			+.353			+.408
				2 Range				.032	.031		.205			.623			.745
E[1]	312–13	2	Air	2 Average				.139	.152		.160		.158				.168
				2 Range				.009	.011		.027		.050				.054
F[1]	459–13	2	Air	1				.065	.112				.096				
G[1]	1079–12	2	Air	6 Average	.087	.094	.102	.108	.142				.180				
				6 Range	.026	.025	.058	.046	.053				.046				

G[1]	1079–12	3	Air	2	Average	.115	.141	.178	.180			[d].262				
					Range	.010	.018	.008	.004							
G[7]	442–13	2	Air	2	Average				.169		.198			.229				.252
					Range				.025		.006			.002				.008
H[2]	901–12	3	Air	2	Average	.058	.070	.082	.084	.128				.156				
					Range	.002	.004	.001	.001	.001				.002				
I[1]	1208–12	3	Air	1, average					.155	.199			.289					
K[1]	788–12	2	Air	2	Average	.152	.203	.221	.222	.277				.327				
					Range	.019	.016	.018	.021	.010				.005				
L[1]	774–12	3	Air	2	Average	.136	.171	.190	.200	.239				.336				
					Range	.016	.047	.058	.064	.069				.138				
M[1]	669–12	3	Air	2	Average	.119	.162	.174	.181	[d].234				[d].301				
					Range	.012	.011	.006	.006									
A[1]	345–13	2	Water	2	Average				+.103			+.132			+.179			+.210
					Range				.045			.034			.035			.030
B[3]	303–12	2	Water	1		+.055	+.077											
C[2]	243–13	3	Water	2	Average				+.111	+.109		+.100			+.136		+.164	
					Range				.040	.115		.038			.037		.030	
C[3]	397–13	3	Water	2	Average					+.073			+.199			+.152		
					Range					.005			.009			.018		
D[1]	378–13	2	Water	2	Average				+.104	+.117		+.106			+.137			+.163
					Range				.010	.005		.012			.016			.013
E[1]	312–13	2	Water	2	Average				+.118	+.120		+.114			+.147			+.176
					Range				.006	.010		.007			.013			.002
F[1]	459–13	2	Water	2	Average				+.077	+.123				+.196		+.243		
					Range				.021	.022				.005		.000		
F[3]		3	Water	1		+.090	+.090	+.110										
G[7]	442–13	2	Water	2	Average				+.056		+.061			+.094			+.126	
					Range				.004		.012			.004			.017	

[a] All American Portland cements except L, which is a white Portland, and M, which is a nonstaining cement.
[b] See p. 11.
[c] All changes are contractions except where marked with a plus (+) sign.
[d] Only one result obtained.
[e] Only two results in average.

TABLE 10

Summary of Linear Expansion Tests of Neat Cement Prisms Treated in High-Pressure Steam

Brand of cement	Lab. No.	Type of cement[a]	Test piece	Age when treated (days)	Steam pressure (lbs. per sq. in.)	Periods in steam	Total time in steam (hours)	Linear expansion in per cent of original length
A[1]	345–13	2	1	1	300	1	3	1.88
			2	1	300	1	3	1.85
								Av. 1.86
A[2]	406–13	3	1	1	300	1	3	.13
			2	1	300	1	3	.13
								Av. .13
B[3]	303–12	2	1	5	180	1	5	4.20
			[b] 2	1	180	1	5	4.40
			[b] 2	2	180	2	5	4.80
			3	21	275	1	5	4.20
B[1]	948–12	2	1	1	300	1	3	2.70
C[2]	243–13	3	1	1	300	1	3	.38
			2	1	300	1	3	.39
C[1]	397–13	3	1	1	300	1	3	.09
C[4]	1209–12	3	1	4	300	1	3	.14
D[1]	378–13	2	1	1	300	1	3	5.45
			2	1	300	1	3	4.20
								Av. 4.82
D[3]	.....	3	[c] 1	2	100	1	5	.20
			[c] 1	3	100	2	5	.29
			[c] 1	4	100	4	5	.29
			[c] 1	9	180	6	5	.30
			[d] 2	1	100	1	5	.18
			[d] 2	3	100	2	5	.28
			[d] 2	11	100	7	5	.31
E[1]	312–13	1 or 2	1	1	300	1	3	6.50
			2	1	300	1	3	10.80
								Av. 8.65
E[2]	421–13	3	1	1	300	1	3	.12
			2	1	300	1	3	.12
								Av. .12

[a] See p. 11.

[b] Same test piece was treated second time.

[c] This was same test piece subjected to steam at various pressures for 5 hours each time.

[d] Same test pieces tested at 100 pounds steam for periods of 5 hours each.

TABLE 10—Continued

Brand of cement	Lab. No.	Type of cement[a]	Test piece	Age when treated (days)	Steam pressure (lbs. per sq. in.)	Periods in steam	Total time in steam (hours)	Linear expansion in per cent of original length
F[1]	459–13	2	1	1	300	1	3	(*e*)
			2	1	300	1	3	(*e*)
F[2]	178–192–12	3	*f* 1	1	100	1	5	.09
			f 1	2	100	2	5	.10
			f 1	3	180	3	5	.13
			f 1	6	180	5	5	.13
			g 2	1	180	1	5	.13
			g 2	2	180	2	5	.14
			g 2	3	180	3	5	.21
			g 2	4	180	4	5	.31
F[3]	195–214–12	3	*h* 1	1	100	1	5	.06
			h I	2	180	2	5	.07
			h 1	5	180	4	5	.07
			h 2	1	180	1	5	.09
			h 2	3	180	3	5	.11
F[4]	251–60–12	3	*i* 1	1	100	1	5	.16
			i 1	2	100	2	5	.15
			i 1	4	180	4	5	.16
			i 1	7	180	6	5	.16
G[2]	1080–12	2	1	3	300	1	3	4.30
G[7]	442–13	2	1	1	300	1	3	5.92
			2	1	300	1	3	6.08
G[2]	1081–12	3	1	1	300	1	3	.13
G[1]	1079–12	3	1	1	300	1	3	.12
G[8]	435–12	3	*j* 1	2	180	1	5	.10
			j 1	3	180	2	5	.11
			j 1	7	180	6	5	.14
H[1]	532–12	3	*k* 1	1	180	1	5	.05
			k 1	2	180	2	5	.14
I[1]	1208–12	3	1	4	300	1	3	.13

e Completely disintegrated.

f Same test piece tested at various pressures for a period of 5 hours each time.

g Same test piece tested several times for periods of 5 hours each time.

h Same test piece treated several times for a period of 5 hours each time.

i Same test piece treated several times at various pressures for periods of 5 hours each.

j This test was made after this cement became type 3. Same test piece treated several times for periods of 5 hours each time.

k Same test piece.

TABLE 10—Continued

Linear Expansion of Standard Specification Cement and Mortar Treated in High-Pressure Steam

Brand of cement	Lab. No.	Type of cement	Composition of test piece	Age when treated (days)	Steam pressure (pounds)	Testing periods	Total time in steam (hours)	Linear expansion in per cent of original length
B[3]	303 to 314–12	2	Neat	1	180	1	5	4.7
			1:1 standard sand	1	180	1	5	4.6
			1:2 standard sand	1	180	1	5	3.3

4. RELATION BETWEEN FINENESS OF CEMENT AND SOUNDNESS IN HIGH-PRESSURE STEAM

A cement passing the standard fineness and soundness tests but showing unsoundness in the qualitative high-pressure steam test was separated into that passing the No. 200 sieve and that retained on the No. 200 sieve. A pat was made of the cement passing the No. 200 sieve and treated in steam at 300 pounds pressure for one hour, total time in high-pressure boiler being three hours, and when examined it was found perfectly sound. A mixture of one part cement passing the No. 200 sieve and one part of the material retained on that sieve was then made, from which a pat was molded and subjected to the qualitative high-pressure steam test, with the result that the pat completely disintegrated under treatment. A pat containing a mixture of two parts of the cement passing the No. 200 sieve and one part of the retained material was similarly tested and likewise disintegrated in high-pressure steam, but the disintegration was not as complete as in the 1:1 mixture. Further, the coarse material retained on the No. 200 sieve from a cement that was sound in the qualitative high-pressure steam test was made into a pat and exposed to high-pressure steam, with the result that the pat completely disintegrated. This same cement when tested as received by the quantitative high-pressure steam test showed a 25 per cent increase in tensile strength for the treated cement over the untreated. Many of the routine cement samples that passed the high-pressure steam test were relatively coarse cements, i. e., only

75 to 80 per cent passing the No. 200 sieve. One cement having 79 per cent passing the No. 100 sieve and 61 per cent passing the No. 200 sieve was sound in the high-pressure steam test.

5. EFFECT OF AGE ON THE SOUNDNESS OF CEMENTS THAT ORIGINALLY ARE UNSOUND IN HIGH-PRESSURE STEAM TESTS

About 30 samples of cement, all sound in the standard atmospheric steam test but unsound in the qualitative high-pressure steam test, were stored in air-tight glass jars and retested in high-pressure steam at various intervals. The results of these tests indicate that a cement originally unsound in high-pressure steam will become sound, according to this test, in from two to six months. On some of the cements a number of pats were made at a time when the cement was unsound in high-pressure steam. These pats, which were stored in both air and water, were tested at subsequent intervals, and it was found that most of them passed the high-pressure steam test after storing for from six months to one year. A sample of one cement which was unsound in the standard atmospheric steam test stored in a cotton bag in the laboratory became sound in three weeks; stored in a Mason jar with cover tightly screwed on, it became sound in four months; and sealed in a glass jar from which the air was exhausted, it was still unsound at the end of two years.

V. SUMMARY

The general soundness tests show that some cements mixed neat, which are sound according to the standard specification atmospheric steam test and unsound after exposure in high-pressure steam, exhibit signs of unsoundness when stored under normal conditions in dry air. This unsoundness may require nine months or more to develop where the test pieces are of neat cement.

The tensile strength tests of 1:3 mortar fail to show that a cement passing the high-pressure steam test is superior in cementing value to a cement which does not pass this test but passes the standard specification test. The briquettes made from the cement unsound in atmospheric steam do not show inferiority in strength to those

made of sound cement. A striking feature of these tests at the later periods is the high value attained by two of the cements which were unsound in the atmospheric steam test.

The compressive strength tests of 1:3 mortar in 2-inch cubes show a comparatively low strength at the earlier periods for type 1 cement, which is unsound in the atmospheric steam test, and a high strength at all periods of type 3 cements which pass the high-pressure steam test. In all cases where several samples of the same brand, some classified as type 2 and some as type 3 cement, the test pieces which contain the type 3 cement give higher strength values throughout.

The compressive strength tests of the concretes composed of one part Portland cement to two parts sand and four parts of gravel show a superiority at the earlier periods of type 2 and type 3 cements, which are sound in atmospheric steam and high-pressure steam, respectively, over the type 1, which is unsound in atmospheric steam, and little or no difference in strength between type 2 and type 3 cements at any periods.

There is no consistent relation existing between the strength of type 2 and type 3 of the same brand, sometimes type 2 being stronger and at other times type 3 is stronger. There is a large range in the strength of samples of the same brand received at different times irrespective of the type, and a considerable range in the different brands both for type 2 and type 3. It was noted that cylinders tested in the winter and spring months consistently gave lower values than similar cylinders tested in the summer and fall, but no explanation can be offered for this variation. It is interesting to note that one of the cements giving one of the strongest concretes throughout was taken from a delivery rejected on account of unsoundness in steam and is a type 1 cement.

The results of the tests of linear change of neat cement prisms of both type 2 and type 3 cements as a whole show no difference that could be attributed to the type of cement when the prisms are stored in air and water. There is more variation between the different brands than between different types of the same brand. However, in one case a neat cement containing type 2 cement (marked D^1) at four months began to expand in air and continued

to expand to a great degree up to the last period measured. This test prism also began to warp and show signs of disintegration. Several of the other prisms containing type 2 cement showed some warping, but no prisms containing type 3 cement exhibited any warping or other signs of unsoundness. (See Fig. 6.)

The treatment of neat cement prisms in high-pressure steam showed an expansion of from 1.86 to 10.80 per cent for type 2 cement (in some cases the prisms completely disintegrated), while prisms containing type 3 cement expanded in high-pressure steam from less than 0.1 up to 0.31 per cent. Increasing the pressure from 100 to 300 pounds affects the amount of expansion of the prisms but little, if any. The addition of a small amount of water-repellant compound to the cement does not affect the amount of its change of length when stored in air or water. The addition of sand to a prism containing type 2 cement reduces the amount of expansion in high-pressure steam for a 1:1 mortar to 96 per cent of that of the neat, and for a 1:2 mortar to 69 per cent of the neat, all being subjected to the same high-pressure steam treatment.

Seventy per cent of a total number of 51 brands of cement tested passed the high-pressure steam test.

Of cements normally unsound in the standard atmospheric steam or high-pressure steam test, if the finer sized particles are removed and tested separately, they will generally be found more sound than the original cement tested in the same manner, and in many cases they will be found entirely sound. Further, if the coarse particles of a cement which is sound after exposure in high-pressure steam are removed and tested separately, they may be found to be unsound in this test. While fineness is not essential to soundness, it appears to be the coarse particles of a normally unsound cement which cause the expansive action and the cracking and disintegration of the pat.

A cement originally unsound in the high-pressure steam test will usually be found sound if exposed to this test after aging from two to six months.

If a cement which will not meet the requirements of the high-pressure steam test is mixed with water and formed into a pat,

it sometimes becomes sufficiently sound to pass the high-pressure steam test, if the pat is stored from six months to a year in either air or water prior to exposing to high-pressure steam.

The maximum tensile strength of sound cement exposed to steam appeared to be attained at a pressure not exceeding 150 pounds per square inch; but this may vary with different brands and different durations of the steam treatment. Type 2 cement begins to fail when subjected to steam at a pressure as low as 25 pounds.

VI. CONCLUSION

1. The high-pressure steam test should be made on all cements that are incorporated in cement, mortar, or concrete products that are to be cured in steam at pressures above atmospheric.

2. The high-pressure steam test may be of value as forecasting the behavior of neat cement or a very rich mortar when exposed under normal conditions in dry air, but it will not forecast the behavior of cements in concretes as normally exposed.

3. The cement passing the high-pressure steam test is not superior in cementing quality, as determined from the compressive strength of concretes, to cement that fails to pass this test.

4. The cement passing the high-pressure steam test does not make more permanent or durable concrete than cement which meets the requirements of the standard specification but fails to pass this test.

5. Cement failing to pass the standard specification atmospheric steam test but meeting the other requirements of the standard specification shows in some instances a normal strength in concrete.

6. For practical work under normal conditions of construction, the results of this investigation fail to show that the high-pressure steam test is of value as a means of determining the ultimate soundness of concrete.

WASHINGTON, March 16, 1915.

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AN AIR ANALYZER FOR DETERMINING THE FINENESS OF CEMENT

BY

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and

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Bureau of Standards

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By J. C. Pearson and W. H. Sligh

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I. INTRODUCTION—GENERAL DISCUSSION OF ELUTRIATION METHODS IN THE MECHANICAL ANALYSIS OF CEMENT

The fineness of cement is one of its most important and at the same time one of its most indefinite characteristics. Its importance is recognized in the tendency toward higher fineness requirements in cement specifications and in the general belief that the finer a cement is ground the greater its cementing value. Its indefiniteness is due to the almost universal method of determining fineness by means of the No. 100 and No. 200 sieves. The inadequacy of these sieves is evident when one considers that at least 75 per cent of the total cement is required to pass the No. 200 sieve. It is also well known that a considerable portion of the cement passing the No. 200 sieve is comparatively inert because the larger particles in this portion are still too coarse to be readily acted upon by water.

What is needed, therefore, is some means of determining the amount of hydraulically active material in cement. At the present time, however, we do not know what size of particles should be regarded as the upper limit of active material, and thus the logical mode of procedure would seem to be first to develop some method of separating still further the "fines" from the No. 200 sieve, and then to establish a dividing line between inert and active particles.

The terms "flour" and "impalpable powder" are frequently used to designate the hydraulically active material. It is believed preferable to limit these terms to that very fine portion of cement beyond the finest perceptible grit, which probably does not constitute all of the hydraulically active material.

An endeavor has been made at the Bureau of Standards to develop an analyzer capable of giving a mechanical analysis of that portion of cement passing the No. 200 sieve. Such an analysis it appears can best be made by elutriation methods, in which the desired separations are accomplished by washing or blowing the fine material from the coarse. Two types of apparatus need thus be considered, one employing a liquid and the other a gas. In common with most investigators of this subject we believe that a gas or air analyzer is particularly adapted to cement and possesses distinct advantages over the liquid type. The disadvantages of the latter appear to consist largely in the inconvenience of recovering the separated material from the liquid and the difficulty of separating the very fine particles. On the other hand, the liquid type is probably better adapted to making a number of separations in one operation, which compensates to some extent its aforementioned disadvantages. While our own experience is limited to the air analyzer, we believe that either type is adapted to cement analysis, and provided certain essential features are embodied in their construction, satisfactory elutriators of very different forms and dimensions can be devised.

Our experience has indicated that the most important factors in elutriator design are:

1. The apparatus should insure as far as possible a constant velocity and uniform stream lines in the fluid as it passes through the separating chamber.

2. The fluid should not be appreciably retarded by the resistance of the material under examination or by constrictions or obstructions in that part of the apparatus beyond the separating chamber unless the amount of such retardation can be determined by pressure gages or compensated by special devices.

3. All particles of the material should be completely and continuously exposed to the action of the fluid, so that any which are capable of passing through the separating chamber may have every opportunity to do so.

4. The separating chamber should have no places of lodgment for material.

5. The apparatus should be capable of separating fair-sized samples, preferably 25 g. or more. Thus, representative samples

are more nearly insured and the percentage error in the separations is reduced.

More difficult than the mere design and construction of a satisfactory elutriator is its calibration or standardization. The mechanical analysis involves separations in terms not only of percentages but also of sizes, and the determination of the size of very small and irregularly shaped particles can be most readily accomplished by averaging microscopic measurements on a large number. Herein lies the one great obstacle to the furtherance of elutriation methods, for if the fineness curves of different cements are to be at all comparable the sizes of separation must be determined with considerable accuracy. It is not sufficient simply to state that the average diameter of a lot of particles which lie on the dividing line between two fractions is so many thousandths of an inch, or so many hundredths of a millimeter, but it is necessary to define what is meant by the diameter of an irregular particle, and to state explicitly how the diameters are measured. For example, if the diameters of a number of particles as seen in the microscope are measured in one direction without regard to their orientation (which is perhaps the easiest and most direct method) the average diameter so determined will be very approximately the mean of the average length and breadth of the particles as seen in the microscope. This average diameter, however, is greater than the cube root of the product of the average length, breadth, and thickness of the particles, which is generally taken to be the true mean diameter and the true index of "size" in the sense of volume. But the measurement of three diameters of microscopic particles is exceedingly laborious, and the most one can expect for practical purposes is to establish some reduction factor which will give the true mean diameter when applied to the simpler measurements.

Still another condition enters which magnifies the differences in these systems of measurement: The separation of powders by flotation methods obviously depends on the "floating power" of the particles, a property which presumably bears as close a relation to shape and surface condition of the particles as to their actual size and weight, and we may therefore anticipate a greater range in diameters of particles so separated than, for example, in uniform sieve separations.

II. SCOPE OF THE WORK

The chief aim of the work in developing an air analyzer for cement at the Bureau of Standards has been, first, the construction of an apparatus designed on the principles already set forth, and second, the calibration of the apparatus in such manner as to give reliable mechanical analyses of different brands of cement. After more than two years' investigation sufficient progress has been made to warrant publication of the results thus far obtained, but it must be admitted that only the more important phases of the entire problem have as yet been considered. The present status of the investigation may be best described by stating that the analyzer is capable of separating cement into almost any desired fractions, of which the quantities can be determined with the same accuracy as those obtained by sieving and the sizes of separation can be determined with fair accuracy sufficient for purposes of comparison.

III. REVIEW OF PREVIOUS TYPES OF ELUTRIATORS WHICH HAVE BEEN USED OR PROPOSED FOR THE MECHANICAL ANALYSIS OF CEMENT

A cooperative attempt to develop a standard elutriator for cement was undertaken several years ago by a committee of the International Association for Testing Materials. The problem of this committee was set forth as the "Determination of the simplest method for the separation of finest particles in Portland cement." Reports of progress were made by the chairman of the committee in the proceedings of the association for 1906, 1909, and 1912, and these reports were supplemented by papers presented by members who participated in the investigation. In these reports and papers a systematic study of the problem has been made, and in them will be found a more complete discussion of several of the types of apparatus briefly described in the following paragraphs.

1. GOREHAM'S FLOUROMETER

The following description of this apparatus (Fig. 1) is given in the reports of the Brussels Congress of the International Association for Testing Materials:[1]

It consists chiefly of two tubes R and r, the latter inside the former. The outer zinc tube R has a diameter of 8 cm and is closed at the top and tapered at the bottom. It fits air-tight into a tapered receptacle in which the cement to be tested is placed. The tube r, placed inside R, is carried air-tight through the cover of R and reaches as far as the narrowest part of the vessel K. The end piece is notched so as to pre-

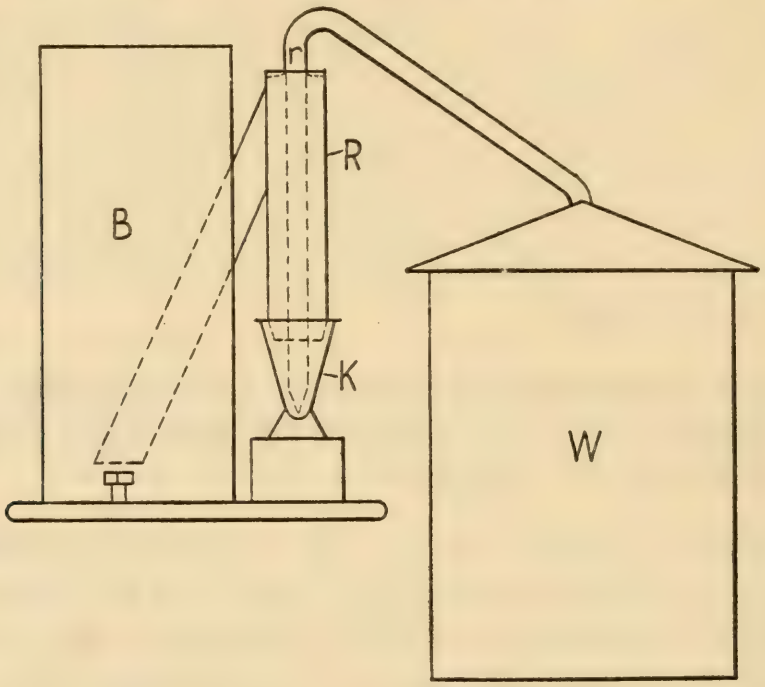

FIG. 1.—*Goreham flourometer*

vent the narrow space between the two tubes from being choked with cement. Tube R carries at half its height an uptake tube which ends inside a large receptacle B. The air is driven through the inner tube from an aerometer W at a fixed pressure and passes through the notches; then it strikes against the tapered sides of the vessel K and stirs up the cement, of which the receptacle contains about 40 grams. The flour is carried off by the current of air, and the greater portion settles in receptacle B. At the end of the test the cement residue is weighed.

This apparatus has more good points in its favor than a number of later types and is to be recommended especially for its simplicity. The main criticism of its operation would appear to be

[1] Determination of a Uniform Method for the Separation of the Finest Particles in Portland Cement by Liquid and Air Processes. Report by M. Gary, chairman of committee 30, Brussels Congress, Int. Ass'n Test. Mat'ls, 1906.

a considerably retarded air stream at the beginning of the separation, the air flowing more freely as the residue diminishes. A less important point is the fact that the "fines" leave the separating chamber *R* from one side of the latter only, whereas the delivery should preferably be symmetrical around the tube. The latter should also be high enough to avoid the removal of excessively heavy particles by impulses from the bottom.

2. THE GARY-LINDNER APPARATUS

The Gary-Lindner apparatus is perhaps the best-known elutriator for cements that has been devised, and its description, as given by Gary, one of its inventors, is also to be found in the International Association Reports of the Brussels Congress, 1906.[1a]

This apparatus, which also depends on the action of a current of air, but arriving at a more complete granulation, is shown in Fig. 2. It consists of three good-sized glass tubes *a*, which are connected with each other and which end in glass funnels. Small glass tubes for conveying the air, and extending almost to the bottom, are fused into the funnel tubes. Twenty grams of the powder to be tested, which must be thoroughly dried beforehand, are placed in the first funnel *I*. An air blast at a pressure of 100 mm (height of water) is then blown in. The air pressure for each funnel is regulated by glass cocks and is read off on a U gage. The funnels *I*, *II*, and *III* come successively into operation. Finally a portion of the powder will remain in each funnel, and the flour, which arrives as dust at the end of the third glass tube, is caught in the receptacle *IV*. The process admits of a granulation of four fractions of the cement powder, which are not separated exclusively with regard to the size of the grains, but nevertheless show relative characteristic differences.

Fig. 3 is a photograph of one of the Gary-Lindner separators, which gives a somewhat better idea of its proportions. Our experience with this apparatus bore out the experience of others who had tried it in this country in that we were unable to obtain satisfactory separations. Perhaps better results might have been obtained if detailed instructions had been available for the operation of the apparatus, but after some study of its behavior we became convinced that this type of elutriator was not adapted to quantitative separations. By referring to the essential features of a satisfactory elutriator enumerated on page 5, it will be seen that the Gary-Lindner separator fails particularly in the fourth requirement, and to some extent in the first and second. Blown material is certain to lodge at the junctions of the tubes *a*, for it

[1a] See note 1, p. 8.

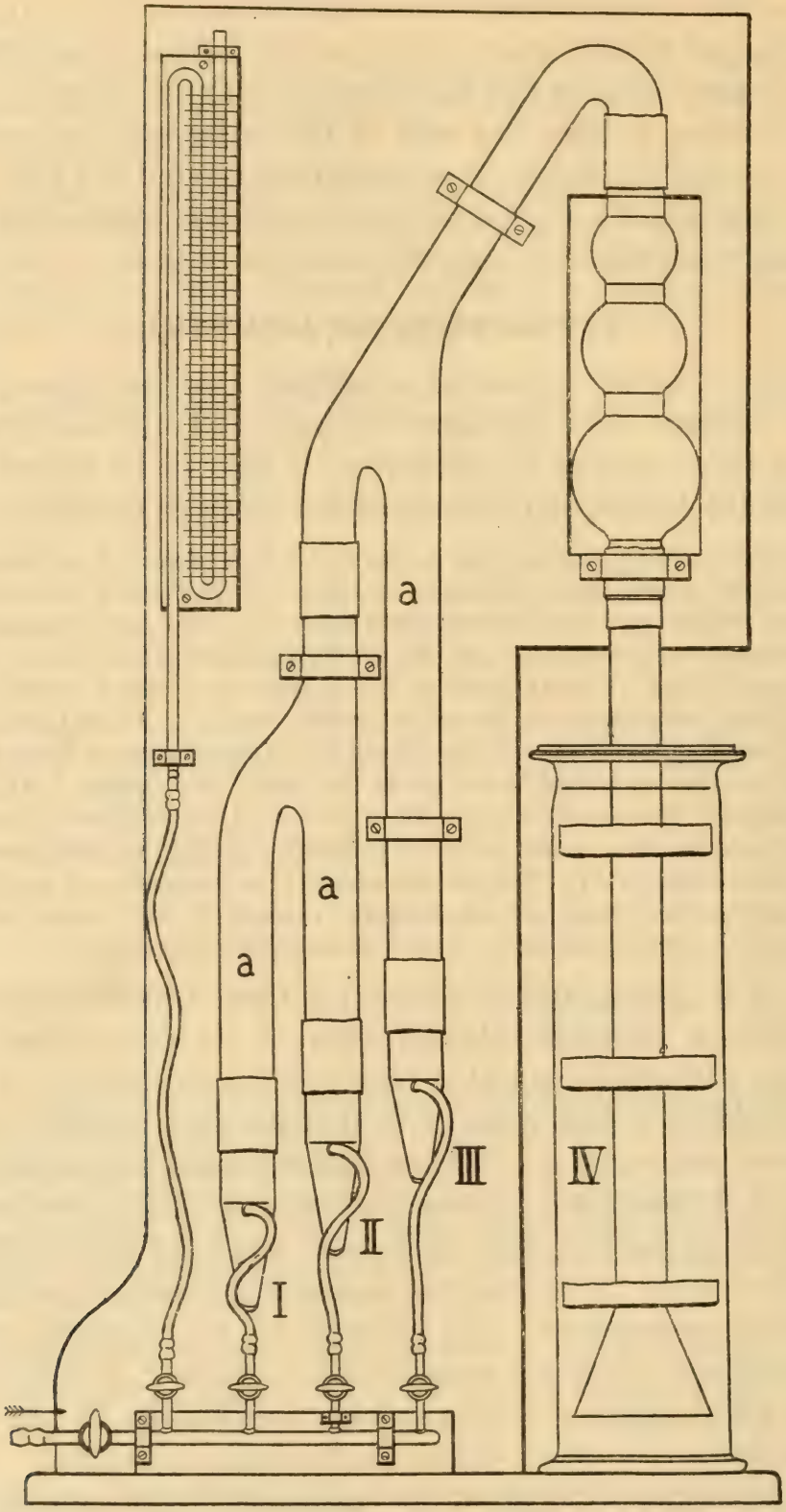

FIG. 2.—*Gary-Linder apparatus*

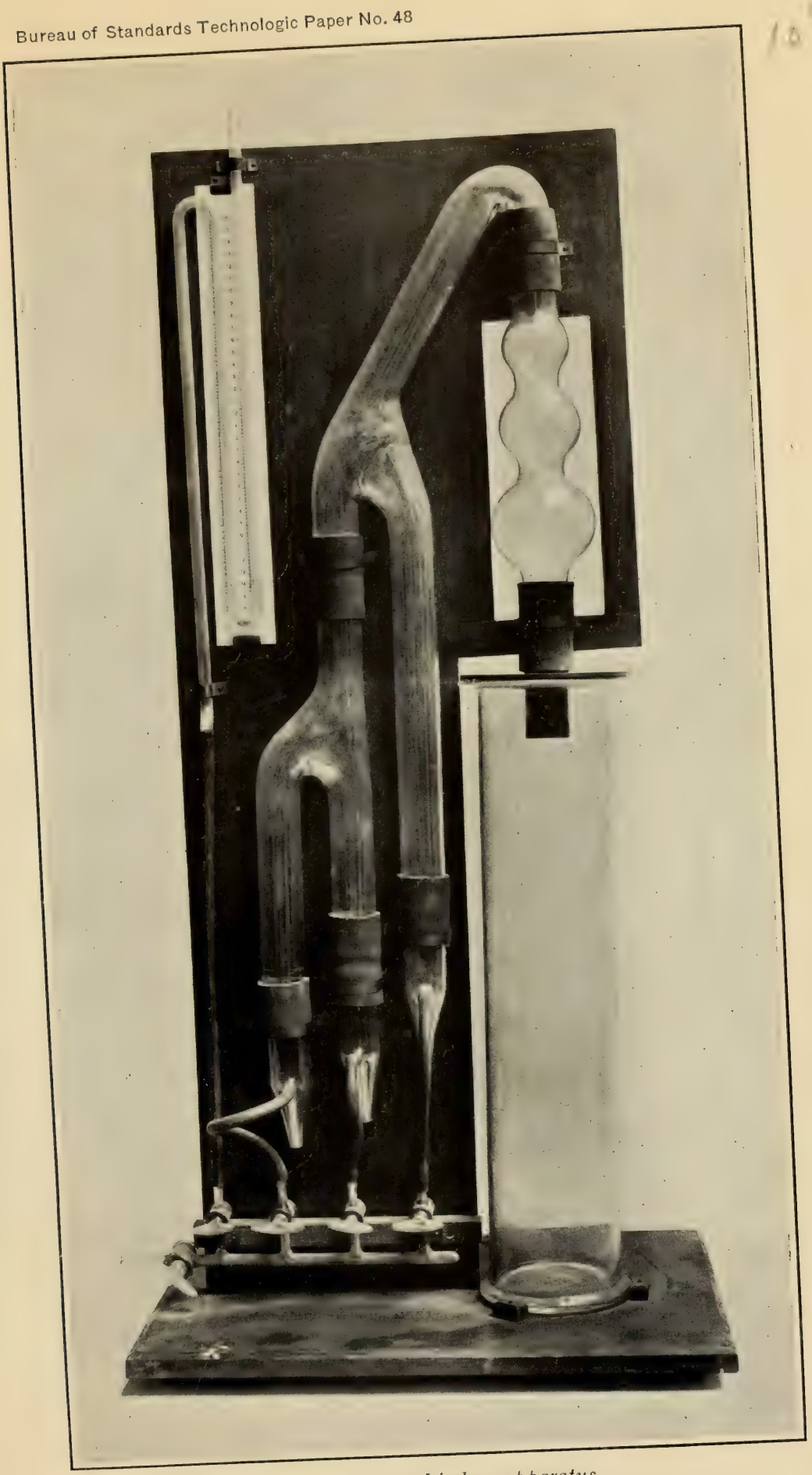

FIG. 3.—*Gary-Lindner apparatus*

is practically impossible to avoid shelves at these points, and the inclined tube connecting with the vessel *IV* will effectually prevent any pure separation of material to the right and left of this point. It has been our experience that any departure from the vertical in the walls of the separating tubes is an undesirable feature, tending to destroy the purity of the separations and adding to the difficulties of keeping the apparatus clean.

3. CUSHMAN AND HUBBARD'S AIR ELUTRIATOR

This apparatus was designed primarily for the separation of rock powders, and is described in the Journal of the American Chemical Society for 1907.[2]

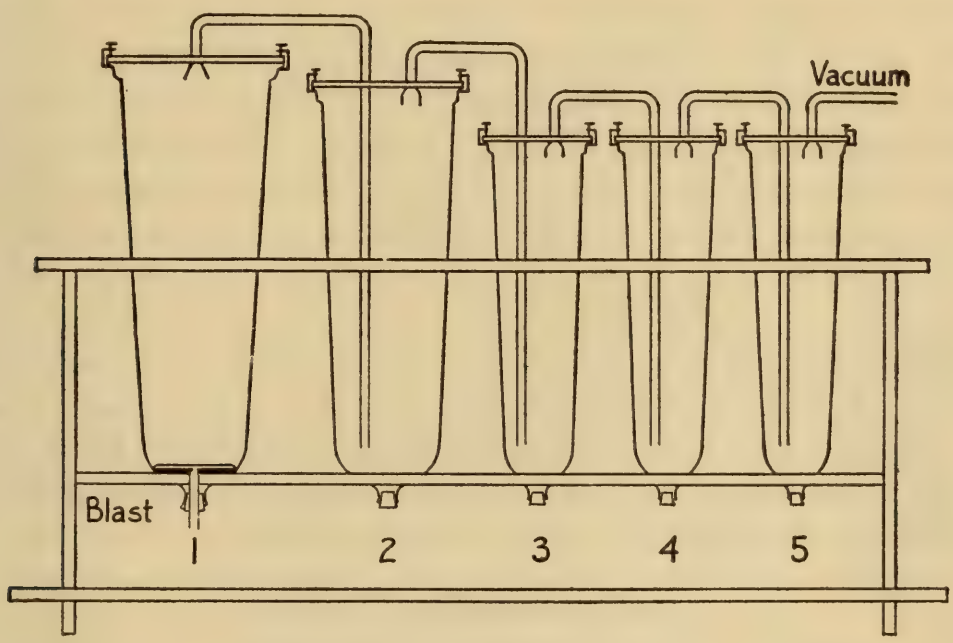

FIG. 4.—*Cushman-Hubbard elutriator*

The apparatus consists of five percolating jars set in a wooden frame and connected by tubes of glass passing through close-fitting caps tightly clamped to the jar tops, as shown in Fig. 4. The first jar is of 3 gallons capacity, the second 2 gallons, and the third, fourth, and fifth, each 1 gallon. In the bottom of No. 1 is placed a flat spiral tube closed at one end but with a number of very small openings through small jets soldered into the upper surface of the spiral at an angle of about 30°. The open end of the spiral passed through a tightly fitting rubber stopper inserted in the neck of the jar and is connected to the source of air supply. An inverted funnel tube whose stem passes through another rubber stopper fitted in the cap at the top of the jar is connected to a glass tube which passes in a similar manner nearly to the bottom of No. 2. An inverted thistle tube connects No. 2 with No. 3 in like manner, and so

[2] Cushman and Hubbard, Air Elutriation of Fine Powders, Jour. Am. Chem. Soc., **29**, p. 589, 1907.

on through Nos. 3 and 4, the exit tube of No. 5 being connected to a vacuum. It is possible to tie pieces of fine linen lawn over the mouths of the inverted thistle tubes, but in our own work this has not been done except in the final exit in No. 5. Rubber stoppers close the necks of the jars and are removed only when it is desired to draw off the charges of powder which have accumulated during a run. A charge of oven-dried powder not exceeding 1 kg is placed in jar No. 1. Blast and vacuum are then turned on and adjusted so that a steady stream of air passes through the powder with sufficient force to raise a dense white cloud which assumes a vortex motion as it ascends, owing to the arrangement of the air jets. The heavier particles continually fall in a ring near the walls of the vessel, where they build up until caved in by the air jets, while the lighter particles are carried into No. 2 through the funnel tube. Here the heavier portions are retained while the lighter pass into No. 3, and so on, the cloud in each succeeding jar becoming less dense. If properly adjusted there is but little loss in No. 5, although the powder here is so fine that no trace of grit can be noticed when it is placed between the teeth.

The Cushman and Hubbard elutriator was used mainly to give only very rough quantitative separations of powders and is obviously incapable of the pure separations which are required for the mechanical analysis of cement. Even if the principle of this elutriator could be adapted to making a number of separations in one operation, the order of the separating jars must evidently be from small to large, since the accumulation of successive residues composed of smaller and smaller particles must depend upon diminishing rather than increasing air velocity through the system. The chief difficulties to be overcome in the construction of such an apparatus are the avoidance of places of lodgment for material in the tubes connecting the separating chambers and an adequate control of the air flow in all parts of the system.

4. THE PETERSEN APPARATUS

This apparatus is a modified form of Schöne's levigating funnel, originally used with liquids, but adapted for and used with air by Petersen in his cement investigations.[3] A diagram of the essential parts of the apparatus is shown in Fig. 5 and its description is quoted below:

The air enters at *a*, passes through the cockpiece *h*, the rubber tube *d*, the bent glass tube *e*, and the rubber tube *f*, up into the funnel *T*, where the levigation takes place. The cockpiece is situated at the lateral tube with the cock *c* in connection with the pressure gage *m*. The sections of the tubes *b* and *c* are of the same diameter

[3] Determination of the Simplest Method for the Separation of the Finest Particles in Portland Cement by Liquid and Air Processes. Appendix to the committee's report, M. Petersen, 5th Cong. Int. Ass'n Test. Mat'ls, Copenhagen, 1909.

as the clear opening in the corresponding glass tubes, so that the air meets with no resistance. By means of the cock *b* the air current can be effectually and quickly cut off, when the residue is removed from the funnel after the levigation. Oil of turpentine, which is sufficiently mobile, is applied in the pressure gage. The air current required for the experiments is produced by means of a centrifugal blower which is placed in connection with the cockpiece *h* by means of a rubber tube. A slide valve is inserted directly in front of the rubber tube, by means of which the air current can be regulated so that a constant height of pressure can be maintained in the pressure gage.

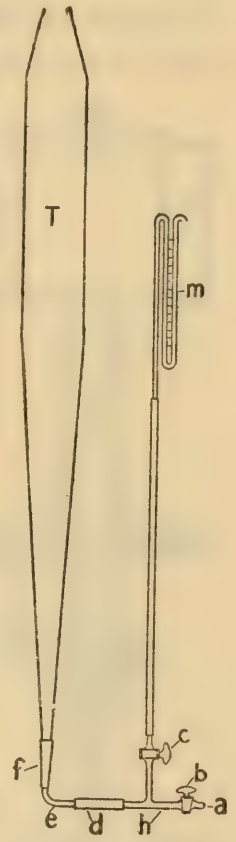

FIG. 5.—*Petersen apparatus*

Elsewhere in the above paper a device is described for introducing the sample of cement into the top of the separating funnel, and another for testing the purity of the separations, but no mention is made of a dust collector of any sort. If the top end of the separating tube was left open during the course of the experiments, the apparatus was certainly in its best working condition, except for the practical disadvantage of exposing everything in the immediate neighborhood to the settling dust. Only 5 g of cement constituted a charge, however, an amount which yields a proportionately small quantity of dust, but the charge is undesirably small for two reasons. The first is that samples of this size may not represent the true average granular composition of the cements as a whole, and second, very small errors in determining the residues, either from accident or from uncertainty in the stopping point of the operation, which in our experience must be determined by the rate of loss and not by the duration of the experiment, will be relatively large when expressed in percentages. Another objection to this "up-blast" type of elutriator is the tendency of the cement to choke in the throat of the separating funnel, which causes fluctuations of considerable magnitude in the air pressure of the supply and requires automatic regulation of the latter. Petersen states that on this account he was unable to use more than 5 g of cement in his analyses.

Whether the residue in the funnel be large or small, it is always being lifted by the incoming air stream, and consequently exerts more or less retardation upon the air delivery, even if the pressure of the supply be automatically regulated. Theoretically,

then, the retardation, and consequently the velocity, of the air through the separating chamber is dependent on the amount of residue left in the funnel; that is, it may be different for different cements, even though the air supply be maintained at constant pressure. This reduction in air delivery may or may not be negligible, depending on the amount of cement used, the sharpness of the cone of the separating funnel, and the normal air pressure used in the experiments, but it can hardly be disregarded. Petersen may have included this effect in his term "choking," but it should be distinguished from the peculiar behavior of the cement which is frequently observed when a sample too large for the air stream to handle readily is first introduced into an elutriator of this type. When the operation is proceeding properly, the whole mass of cement quivers and "teeters" as the air passes through it, gradually removing the fine dust. Very frequently, however, the cement lodges in the cone, the air forces an open "pipe" up through it and blows freely through the separating funnel, leaving the cement undisturbed in the bottom. Continual tapping of the funnel, shutting off and turning on the air supply, and other means must be resorted to of coaxing the cement into action. This contrary behavior of cement is well known to those who have worked with the Petersen type of apparatus, and it constitutes one of the chief objections to the "up-blast" elutriator, for it is a difficulty which increases enormously with the fineness of the separation.

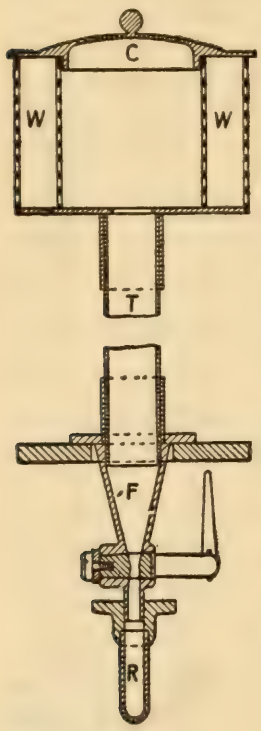

FIG. 6.—*Griffin-Goreham flourometer*

5. THE GRIFFIN-GOREHAM STANDARD FLOUROMETER

This apparatus is described in a number of treatises on Portland cement, the following description being taken from R. K. Meade's Portland Cement:[4]

This apparatus consists of two parts, an aerometer or blower and the apparatus proper, or flourometer. The blower consists of the customary bell and water tank and is merely used to furnish a constant supply of air to the apparatus. The flourometer itself (Fig. 6) consists of a long brass tube *T*, resting upon a stand. The sepa-

[4] Portland Cement, by R. K. Meade, 2d ed., 512 pp. The Chemical Publishing Co., Easton, Pa. 1911

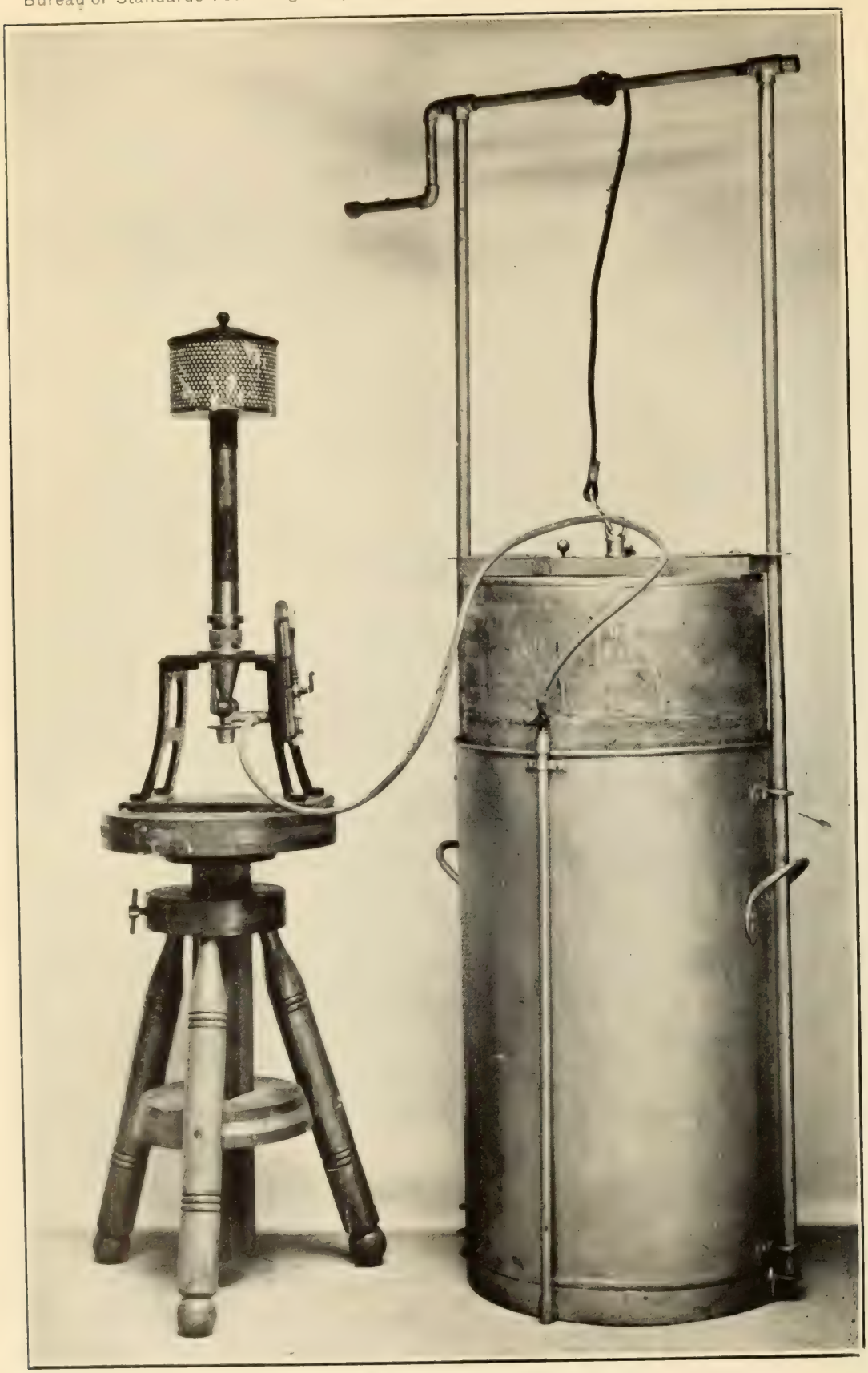

FIG. 7.—*Griffin-Gorcham flourometer*

ration of the coarse and fine particles takes place in this. The tube is surmounted by a double-walled dome *W*, covered with a top *C*. The walls of this dome are perforated, and the spaces in between them, *W*, are filled with cotton. This serves to catch all dust and prevents it being blown into the laboratory. The lower part of the brass tube *T* terminates in a cone-shaped brass casting *F*, which rests upon the stand. A three-way stopcock provided with a pointer to show the direction of the opening is placed at the lower end of the cone and beneath this a glass tube *R*, which serves to catch the coarse particles. The sample of cement should be dried for an hour at 110°. The pointer of the stopcock should be at right angles to the brass tube *T*. The tube *T* is removed, and about 1 gram of the cement is then introduced into the funnel *F*. The bell of the aerometer is now raised to its full extent and the air pressure noted. The pointer of the stopcock is next turned parallel with the tube and the air allowed to blow through the apparatus for 10 minutes. At the end of this time the air pressure is turned off, when the coarse particles from which the cement has been separated drop into the receptacle *R*. This residue is weighed, and the difference of course is flour.

A Griffin-Goreham flourometer was purchased by the Bureau when the work in air analysis was first taken up, and the results of experiments with this apparatus led us to believe that a greater range in separations, as well as better control of the entire process, was desirable. The flourometer serves the purpose of illustrating in a simple manner the principle of air analysis of cements; aside from this its usefulness is limited. In passing it may be pointed out that all the objections which have been brought forward to the Petersen apparatus apply in even greater degree to the Griffin-Goreham flourometer, and the latter was soon discarded in our laboratory in favor of a more suitable design.

6. THE THOMPSON CLASSIFIER

An elutriator using kerosene has been constructed by G. W. Thompson for the study of paint pigments. The apparatus has also been used to some extent for cement analysis and was described in a paper before the American Society for Testing Materials in 1910.[5]

The plan of the Thompson classifier is shown in Fig. 8, the principle of its operation depending on a flow of kerosene at constant head into the upper cone, the overflow passing successively into the larger cones below. The material under examination is first diffused in kerosene so that the particles are completely

[5] The Classification of Fine Particles According to Size, G. W. Thompson; Proc. Amer. Soc. for Test. Mat'ls, **10**, p. 601; 1910.

separated and transferred into the upper cone. The glass tube supplying the kerosene for the separation is then lowered into the cone until it nearly touches the apex, and the current is started. The operation is then practically automatic until the classification is completed. At the end of the operation the residue in each cone is washed into clock glasses with kerosene, allowed to settle, decanted, and washed two or three times with ether. It is then dried and weighed.

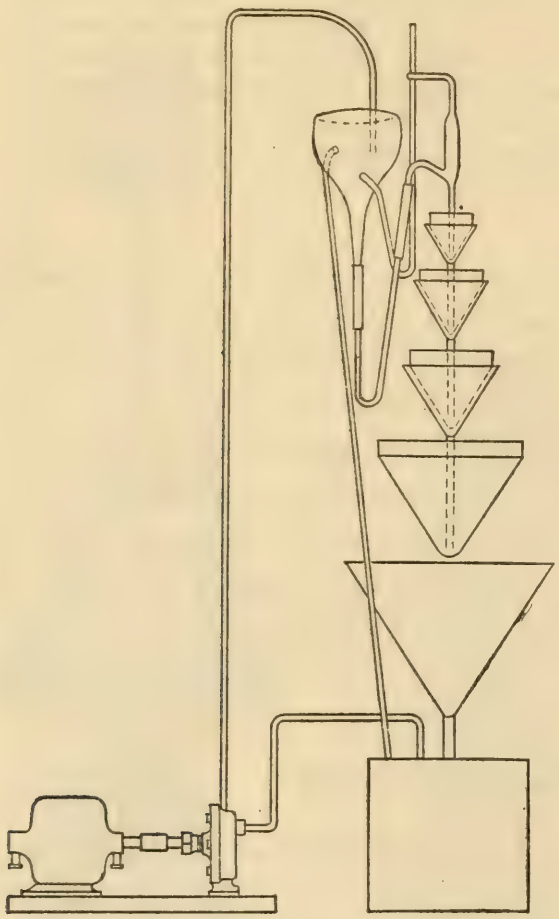

FIG. 8.—*Thompson classifier*

The Thompson classifier possesses the distinct advantage of making several separations in one operation, a time-saving feature which has not yet been successfully introduced into any type of air separator. On the other hand, certain disadvantages suggest themselves, which can only be established as decided objections when more data are available. It has been shown, for example, that the separations of pigments by this apparatus are not wholly reliable, owing either to their incomplete diffusion in the liquid when first introduced into the upper cone, or their tendency to agglomerate in some later stage of their preparation for microscopic examination. There appeared to be less of this difficulty, however, with certain siliceous and crystalline materials,[6] and it is possible that cement would be free from this objection. Another feature of this apparatus which may have a considerable effect on the purity of the separations is the possibility of irregular currents in the cones. The rise of the liquid in all the cones takes place with

[6] Report of Subcommittee J of Committee D-1 on the Testing of White Paints, P. H. Walker, chaiman; Proc. Amer. Soc. Test. Mat., 13, pp. 406-447; 1913.

rapidly diminishing speed, until at the point of overflow all vertical components of the flow have disappeared. It is almost inconceivable, therefore, that there should be uniform stream lines in the cones, in consequence of which the sizes of separation must be less sharply defined than it would be possible and desirable to have them. But it is impossible to state how serious this objection may be in cement analyses. From our experience we should anticipate that even if fractions showing satisfactory quantitative agreement could be obtained in repeated trials, the determination of the size of separation would be more or less uncertain.

7. FERET'S AIR SIFTER

This apparatus is the same in principle as Petersen's apparatus and is described in a paper by R. Feret before the Sixth Congress of the International Association for Testing Materials, New York, 1912.[7]

The paper is devoted to a theoretical study of an apparatus represented diagrammatically in Fig. 9, which is explained by the following excerpt:

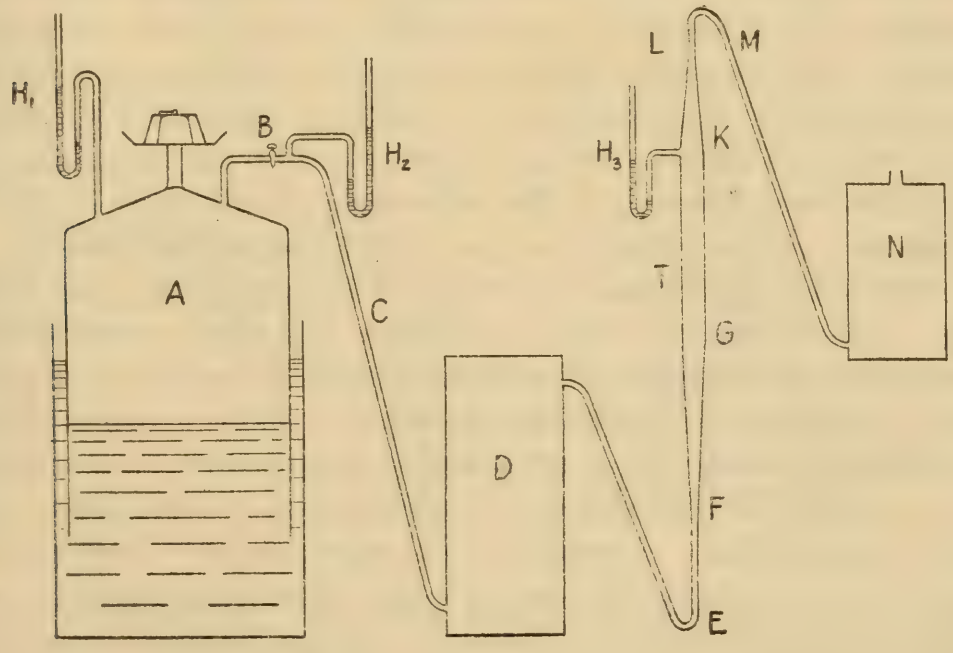

FIG. 9.—*Feret's air sifter*

A is a recipient in which air is maintained at a constant pressure; it communicates by a tap *B*, with a system of pipes *C E*, which lead the air into the sifting chamber

[7] Air Sifting as a Method for the Quantitative Determination of the Finest Particles Contained in Pulverulent Materials. R. Feret; Proc. I. A. T. M., Sixth Congress, Section II, XV2, 1912.

proper T, where the separation between two consecutive classes of grains takes place, the air escaping to the atmosphere through the pieces L M N. D represents a device which may be placed in front of the separator T, in which the carrying off of the grains is to be ascertained, and consisting, for example, of a drying column and other separators. N represents all the various pieces of the apparatus in the rear of the separator T, such as further separators and receivers for the finer dust carried away. H_1, H_2, and H_3 are the three pressure gages showing the excess h_1, h_2, h_3 of air pressure at the corresponding points over atmospheric pressure H.

Feret's studies led him to the almost self-evident conclusion that the limiting size of grains removed by apparatus of this type, or, as we shall hereafter designate it, the size of separation, depends solely upon the flow, and it is the quantity of air delivered which must be controlled and maintained constant. He states further that the regulation of the flow is incorrectly based on the constancy of the pressure of the air supply h_1, unless special precautions are taken to insure the constancy of the resistances in the entire apparatus, but depends rather on the constancy of the pressure in the top of the separating funnel h_3, together with the constancy of the resistance beyond the latter point.

Without going into the derivation of the foregoing result, and assuming it to be true, we are inclined to believe that the general scheme of an apparatus such as Feret has described and studied is unnecessarily complicated as a practical analyzer for cement. Thus we have found that an apparatus can be constructed in which the back pressure in the separating chamber (h_3 in Feret's apparatus) can be reduced to an entirely negligible quantity, at the same time preventing the escape of all dust except that which may be so attenuated as to be invisible. A single pressure gage attached to an air reservoir with an automatic regulator has been found adequate to insure the constancy of the air flow in the separating chamber, at least to such a degree that the variations have a negligible influence on the separations in comparison with other uncertainties. A practical objection has also been pointed out that is common to all the up-blast types of separators operating at comparatively low pressures, viz, such types are adapted only to the examination of undesirably small samples.

8. MACKEY'S APPARATUS

One of the most important investigations ever undertaken to determine the value of fine grinding of Portland cement was carried out some years ago at the University of Kansas by Dr. J. F. Mackey. The results of this investigation became available to us through the courtesy of the Ash Grove Lime & Portland Cement

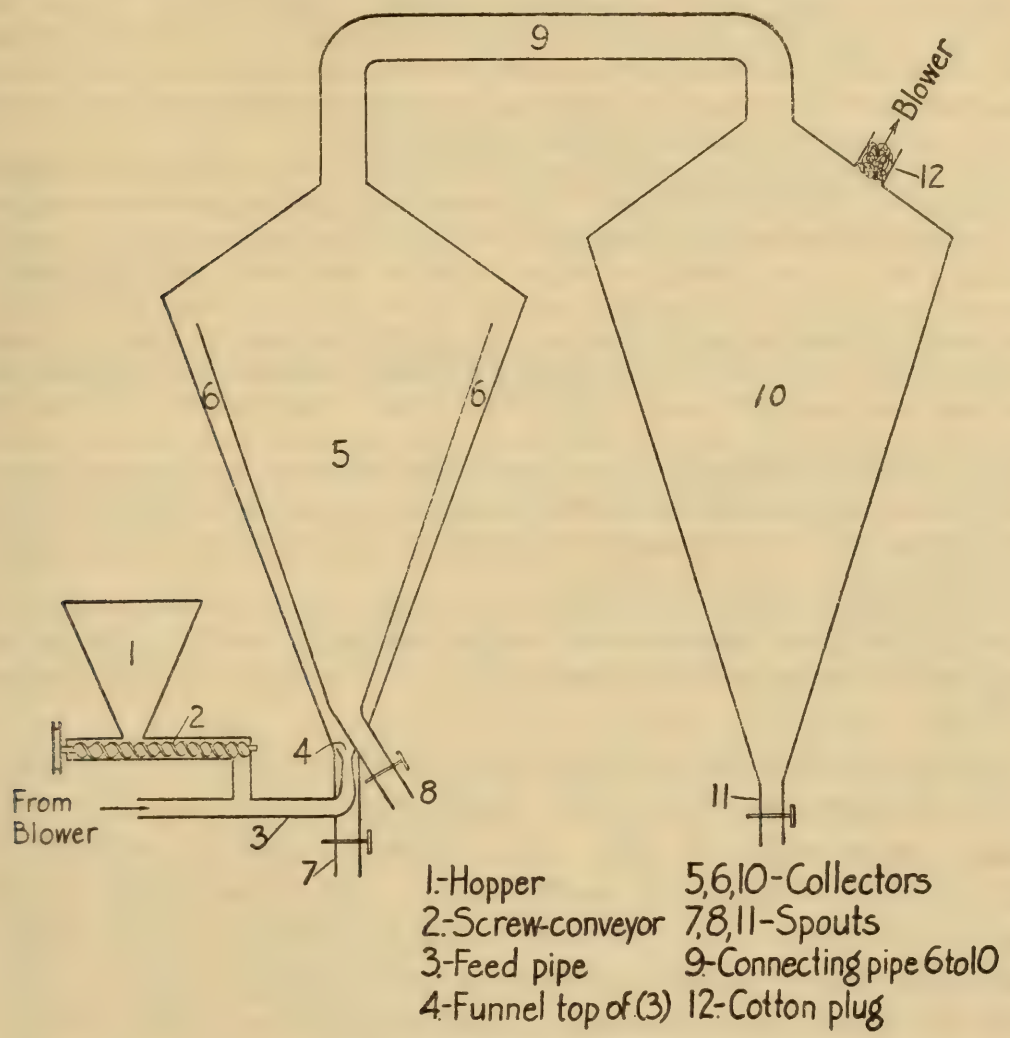

FIG. 10.—*Mackey's apparatus*

Co., of Kansas City, Mo., who established the fellowship under which the work was done.[8] A drawing of Dr. Mackey's apparatus is shown in Fig. 10, and his description of it is as follows:

The large separator was used to obtain large quantities of what is ordinarily termed "flour of cement." The cement to be separated was placed in the hopper (1) and

[8] The Fine Grinding of Portland Cement and the Effect of Hydrated Lime on Portland Cement. Dr. J. F. Mackey.

by means of a screw conveyor (2) fed into the pipe (3), through which a current of air from a blower was passing. By this means the cement was carried into the separators (5), (6), and (10). The arrangement of these conical-shaped separators is shown in the diagram. The cross-sectional area between (5) and (6) gradually increased from the bottom upward, causing the velocity of the air carrying the cement to gradually decrease as it ascended between (5) and (6). Practically all of the coarser particles were dropped in this portion of the apparatus. Any of the finer powder adhering to the walls of this part of the apparatus was removed by gentle tapping.

In the open space above (5) considerable portions of finer material dropped out and were removed from the collector by means of the spout at (8). The finest portions were carried over into (10), which served merely as a collector for these particles. The particles still in suspension were caught in the cotton plug (12) or were carried back to the blower and again sent through the separators.

When the sample had been sent through the apparatus, the products of the various containers were collected separately. The material in (10) was quite free from grit. The whole machine was then cleaned out and all of the materials except the portion collected in (10) sent through as before. Two or three such operations usually removed practically all of the finest powder. There was a small loss due to leakage. In general the contents of (6) contained that portion too coarse to pass a 220-mesh sieve, together with a small amount of finer material; the contents of (5) passed the 220 sieve and contained a small quantity of "flour." The contents of (5) and (6) were then separated in small air elutriators. The separators were arranged in batteries of 8 or 10 and dried air or natural gas blown through under constant velocity. The smaller particles were blown out first, grade C. Then the particles grade B were blown out. The residue was then sieved, and the portion passing the 220-mesh sieve was grade A.

I was not able to obtain a complete separation into a number of fractions with one operation. A special separation was used for each size of particle. The method used, while laborious, nevertheless gave results sufficiently accurate for the purpose in view.

From the foregoing description we understand that Mackey did not expect to obtain very sharp separations with the apparatus represented in Fig. 10, although perhaps satisfactory for the tests that were carried out. The arrangement of the smaller air elutriators is not described in sufficient detail to warrant discussion. Suffice it to say that Mackey obtained very fair agreement in the amounts of the four fractions below the No. 220 sieve. Extensive series of tests were made on these fractions, and valuable information was obtained, but we are concerned for the present only with the identification of the various fractions. Unfortunately Mackey reported only the average apparent diameters of the particles of the different grades, from which it is impossible to deduce the limiting sizes. Without knowing the limiting sizes—that is, the sizes of separation—we can not

derive the mechanical analysis curves, and the microscopic measurements are therefore of little assistance in identifving the separations.

In conclusion of this review of previous types of elutriators, it may be pointed out that there has apparently been no successful attempt to define separations of very fine material in absolute terms, in consequence of which the fractions obtained by one apparatus can not be compared with those obtained by any other. In the work which has been done at the Bureau it has been our particular endeavor to define our separations without reference to the apparatus. In this attempt we have met with a very fair degree of success, and we hope that the methods described in the following pages will encourage a more general use of elutriation processes.

IV. GRADUAL DEVELOPMENT OF A NEW FORM OF AIR ANALYZER

Our experience in air separation of cements really began in the early part of 1912, when a Griffin-Goreham flourometer was purchased and preliminary experiments were made on a number of cements. After a few trials it was believed that this apparatus could be improved and adapted to the examination of larger samples by using a source of air at considerably higher pressure than could be obtained by means of the aerometer furnished with the apparatus. Accordingly, further experiments were made using air from the compressed-air supply in the laboratory at about 2 pounds pressure per square inch. This change necessitated a longer stack, which was constructed of a piece of glass tubing about 1½ inches in diameter and 5 feet long, the upper end being bent in a sharp semicircle to facilitate attaching a dust-collecting sack. Varying the air flow by means of constricted pieces of tubing introduced into the supply line, we were able with this modification to obtain a number of fractions in the fine portion of the cement. In this form the apparatus presented three serious drawbacks—(1) it was noticed that a large amount of fine material collected in the bend of the stack, a considerable portion of which could only be dislodged by taking down the stack and running a cleaner

through it; (2) large pressure variations in the air supply were of frequent occurrence, due partly to the variations in the supply pressure and partly to the choking effect of the cement; (3) there was always trouble from choking and lodging of the cement in the cone at the bottom, this being especially annoying when a small current of air was used for the purpose of blowing out only the very fine particles.

The first of these objections was partly overcome by replacing the stack with another in which an offtake tube was sealed onto the vertical part of the stack at the sharpest possible angle. This stack is still in use as the separating chamber of a later type of analyzer, but the shelf formed at the junction of the offtake, although very narrow, is nevertheless a source of slight error on account of the tendency of material which should be carried off into the collector to lodge there and partly fall back into the coarse residue. It will be shown later that this difficulty can be very easily avoided, yet it constitutes the one glaring fault of the Gary-Lindner apparatus, and in our opinion precludes the use of the latter for quantitative separations of the required purity.

The pressure variations, so far as they were due to variations in the air supply, were avoided by procuring a small May-Nelson two-ring pump driven by a direct-connected Westinghouse one-eighth horsepower motor. A rheostat in the armature of the latter provided means of varying the speed, and up to the limit of its capacity this outfit was the most satisfactory source of air we have ever used, but a somewhat larger capacity was later found desirable. An Eimer and Amend No. 780 blower has proven very satisfactory for this purpose. Small pressure variations were still observed, even after the blower had been installed, and these were found to depend largely on the state of the cement in the separating chamber. It was felt at the time that these pressure variations were unavoidable in this type of separator, which now very closely resembled Petersen's apparatus, as described in the foregoing review.

The third objection to the apparatus—that is, the tendency of the cement to choke and lodge in the cone at the bottom of the separating chamber—proved to be the most difficult of all to overcome, and led eventually to the development of the present form

of analyzer. Numerous attempts were made to avoid this difficulty, one being worthy of special mention. An apparatus was constructed according to the plan shown in Fig. 11. C_1 and C_2 were two brass cones of the same dimensions surmounted by tubes T_1 and T_2, the former connected with the top of the latter by means of a slightly inclined conical tube. T_2 was surmounted by a section of a glass funnel C_3 in the top of which was mounted a cylindrical brass tube T_3, approximately 3 inches in diameter and 3 feet in height. The latter constituted the separating chamber of the apparatus and carried a dust collector on its upper end. The cement to be tested was placed in cone C_1, which was removable. The tube T_1 was partly of glass, to permit observation of the behavior of the cement during the process of blowing. Short lengths of rubber tubing connected to the air supply were attached to the bottom of C_1 and C_2 and closed with pinch cocks to prevent the cement from getting back into the tubes when the air was not flowing. With everything in readiness for the operation, air was first admitted to the cone C_2 and then to the cone C_1. If the air supply were sufficient to handle the cement, the latter was thrown up into the glass tube in violent agitation, and was soon freed from its finest particles. The latter passed over into the tube T_2 and were then further separated, part passing up into the collector, part remaining in suspension in the vicinity of C_3, and the coarsest particles falling back into cone C_2. There was thus a gradual diminution of material in cone C_1, and a gradual accumulation in cone C_2. The obvious purpose of this device was to equalize the retardation of the air stream, thus assuring a more constant flow in the separating chamber, and by using higher pressure with small inlets C_1 and C_2, to induce a more vigorous action in the cement in C_1. Many excellent analyses were made with this device, and photomicrographs of particles showing the sizes and purity of the separations are shown in Figs. 12 to 15. Fig. 16 shows the relative sizes of the largest particles passing a No. 200 sieve.

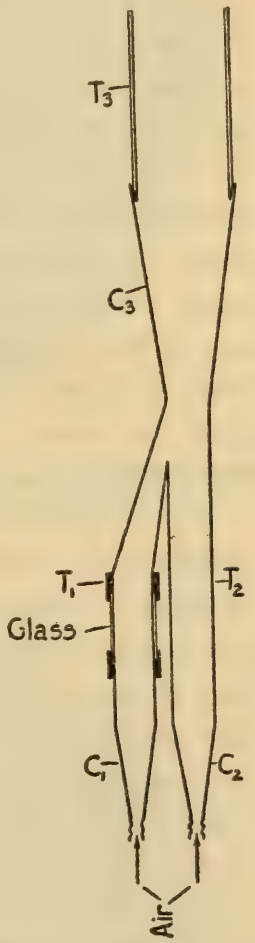

FIG. 11.—*Bureau of Standards double-cone analyzer (discarded)*

Our confidence in this apparatus gradually dwindled, however, when we became assured that it was barely capable of separating less than 30 per cent of a normal cement as the finest fraction obtainable. The size of this separation was in the vicinity of 0.001 inch (0.025 mm.)—that is, the average diameter of the largest particles as seen in the field of a microscope—and the amount of air required to produce this separation was so diminished as to be incapable of handling very finely ground cements. This trouble seemed to depend entirely on the presence of the very fine material, for if the latter were partially removed or the original sample were diluted with a sufficient amount of coarse grains, the process started much more readily. Of course an analysis could be coaxed along by continued tapping, stirring, and by allowing the air to enter in pulses, but for routine analyses such a performance was out of the question. Later experience showed that this difficulty from sticking and clogging might have been overcome, but at that time we came to the conclusion that the up-blast principle was theoretically and practically the weak point in all our elutriators.

It was quite by accident that we hit upon the very simple and satisfactory scheme which has since been adopted in all our later designs. In attempting to blow a considerable quantity of cement out of an ordinary Mason jar with a small air nozzle it was observed that if the nozzle were held stationary and directed into the cement, the latter was blown away, not violently, but by a gradual erosion process, leaving a large conical hole in the mass of the cement. This immediately suggested a new scheme for an analyzer, viz, of sealing up the air inlet in the bottom of the separating cone of the old apparatus and inserting an overhead nozzle *to blow down into the apex of the cone from above.* This was carried out by having a pear-shaped glass bulb blown, into the side of which a bottle-neck opening was made to admit nozzles of glass tubing of different sizes. The open end at the top was also in the form of a wide-mouthed bottle, and designed to fit air-tight to the lower end of a tall glass stack. The original apparatus of this form is still in operation and may be seen in Fig. 18 at *B*. Since this apparatus was constructed improvements have been made in all its parts, but the principle of blowing the air down into the cement from above has been retained and is the chief distinguishing feature of the new analyzer.

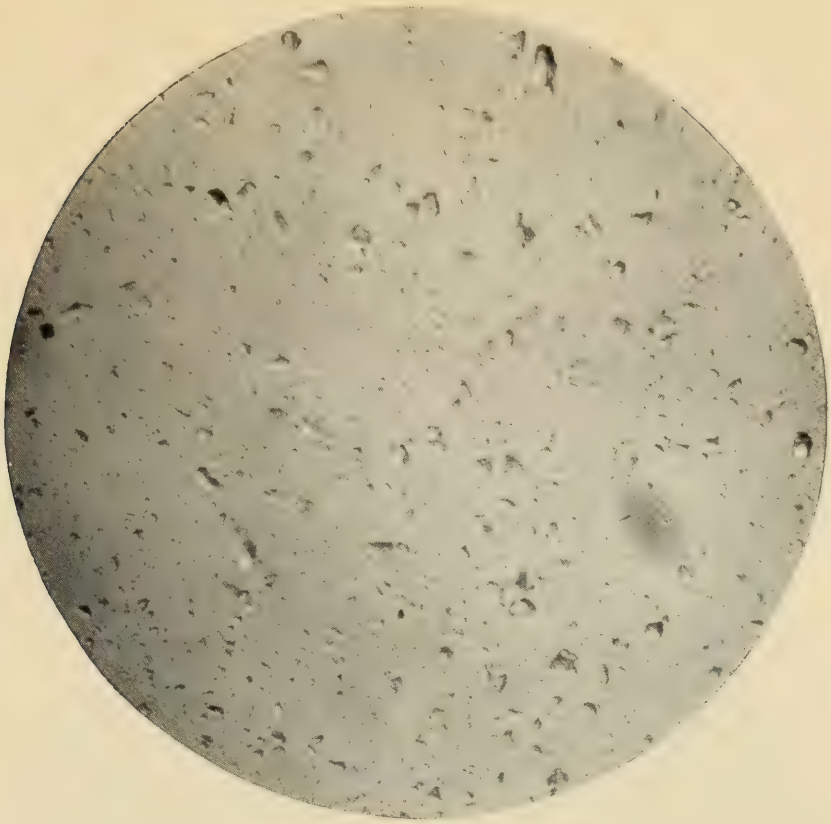

FIG. 12.—*Air-separated cement particles, Grade I, or "flour." Average diameter of maximum particles, 0.0011 inch. Magnification, 150 diameters*

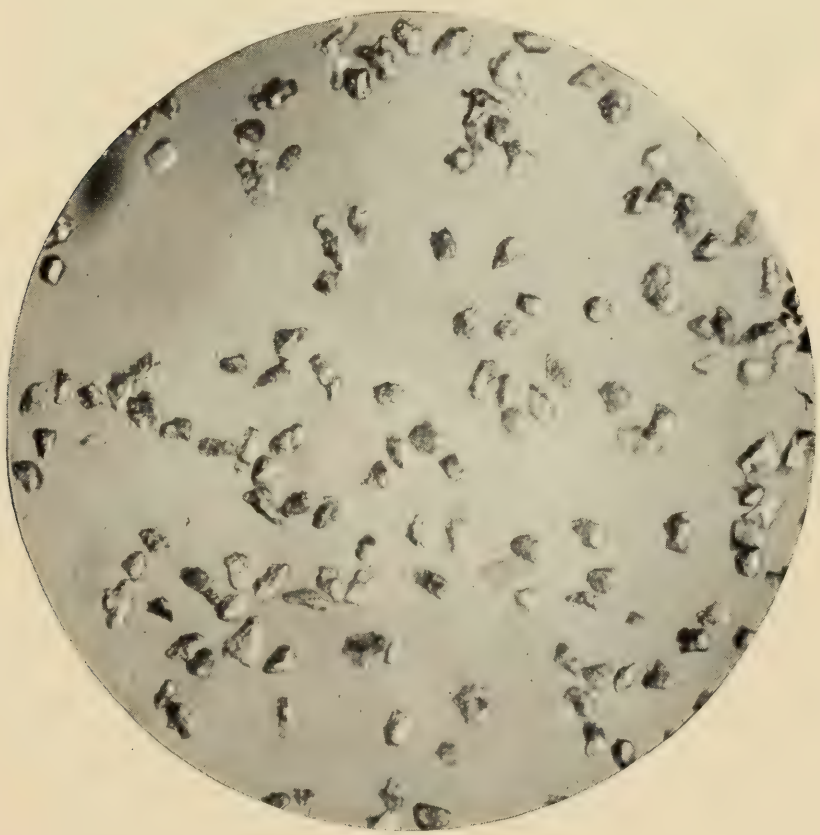

FIG. 13.—*Air-separated cement particles, Grade II. Average diameter of maximum particles, 0.0018 inch. Magnification, 150 diameters*

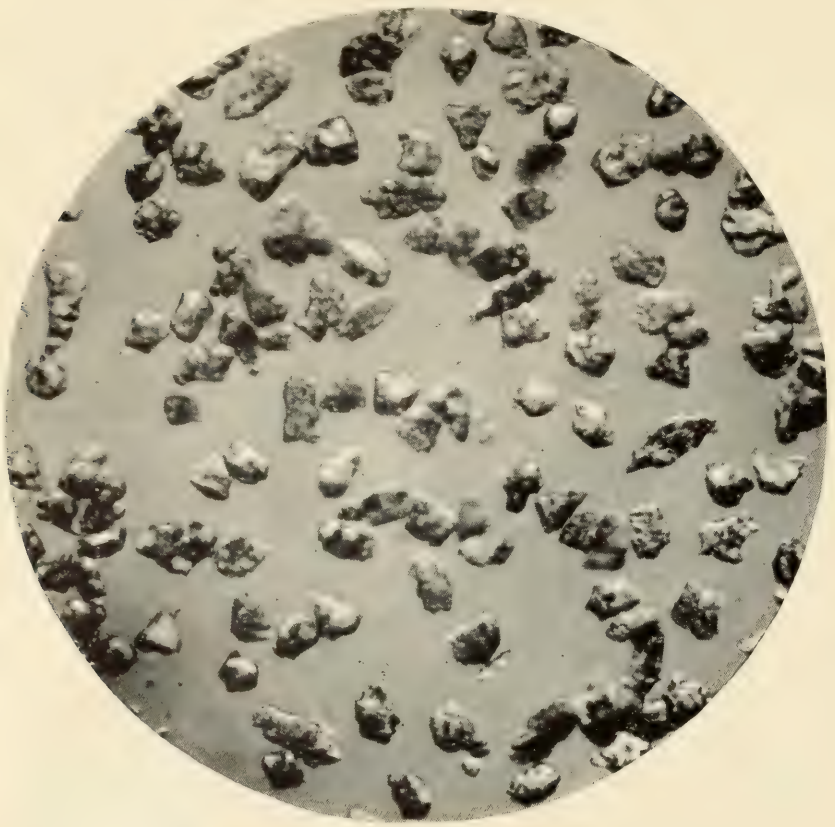

FIG. 14.—*Air-separated cement particles, Grade III. Average diameter of maximum particles, 0.0025 inch. Magnification, 150 diameters*

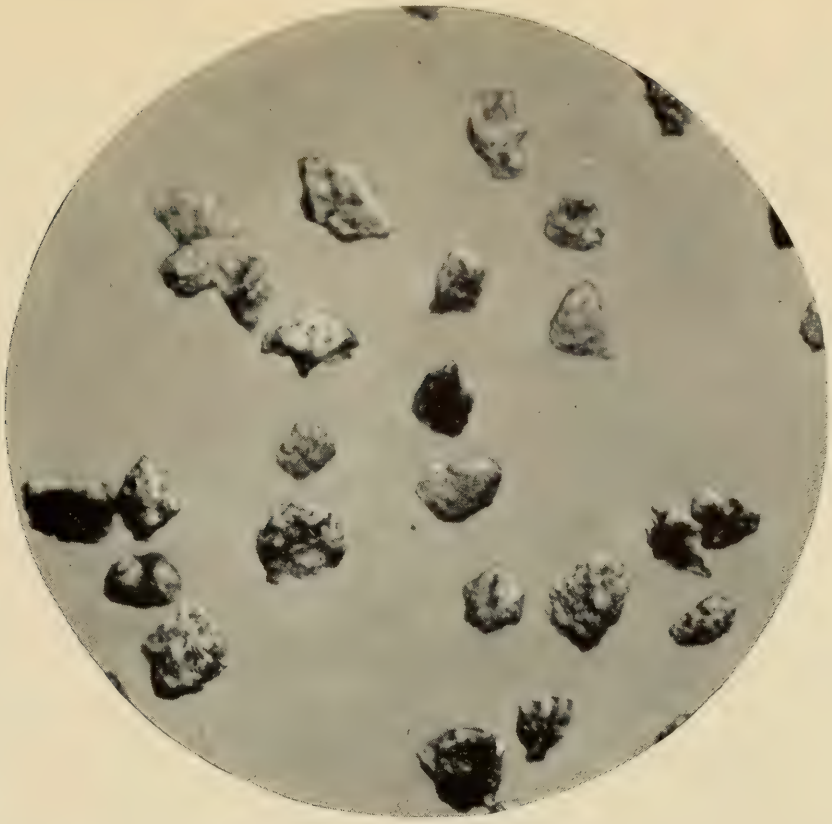

FIG. 15.—*Air-separated cement particles, Grade IV. Average diameter of maximum particles, 0.0033 inch. Magnification, 150 diameters*

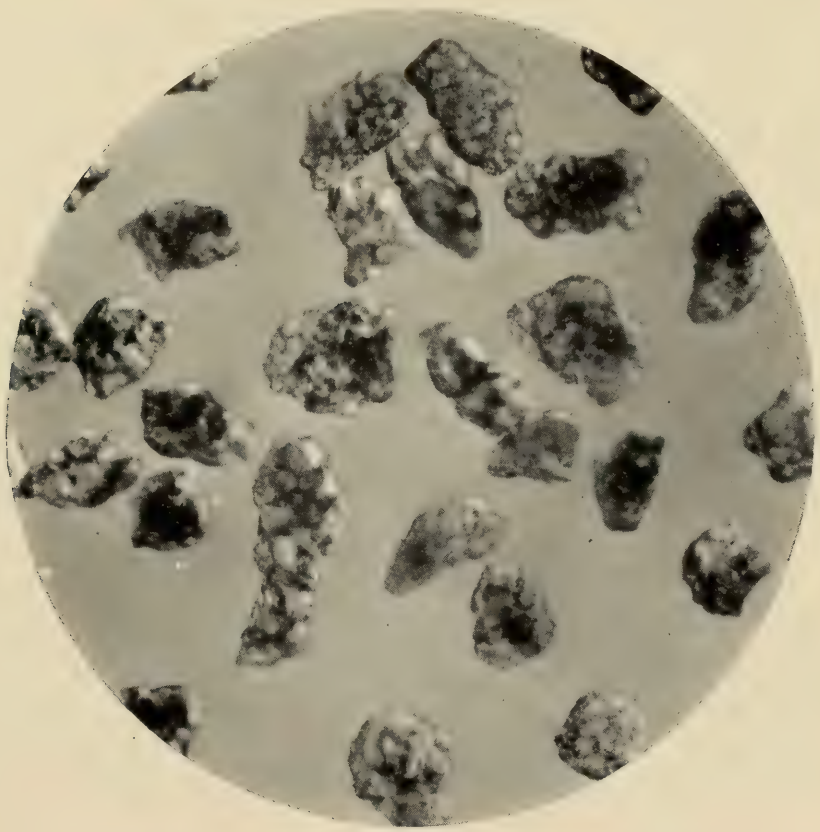

FIG. 16.—*Cement particles passing a No. 200 sieve at the end of the ordinary sieving operation. Magnification, 150 diameters*

V. DESCRIPTION OF THE ANALYZER IN ITS PRESENT FORM

The present analyzer in operating condition is shown in Fig. 17. The analyzer proper is shown at the right of the diagram, and consists of four essential parts—the bulb, with its set of three inter-

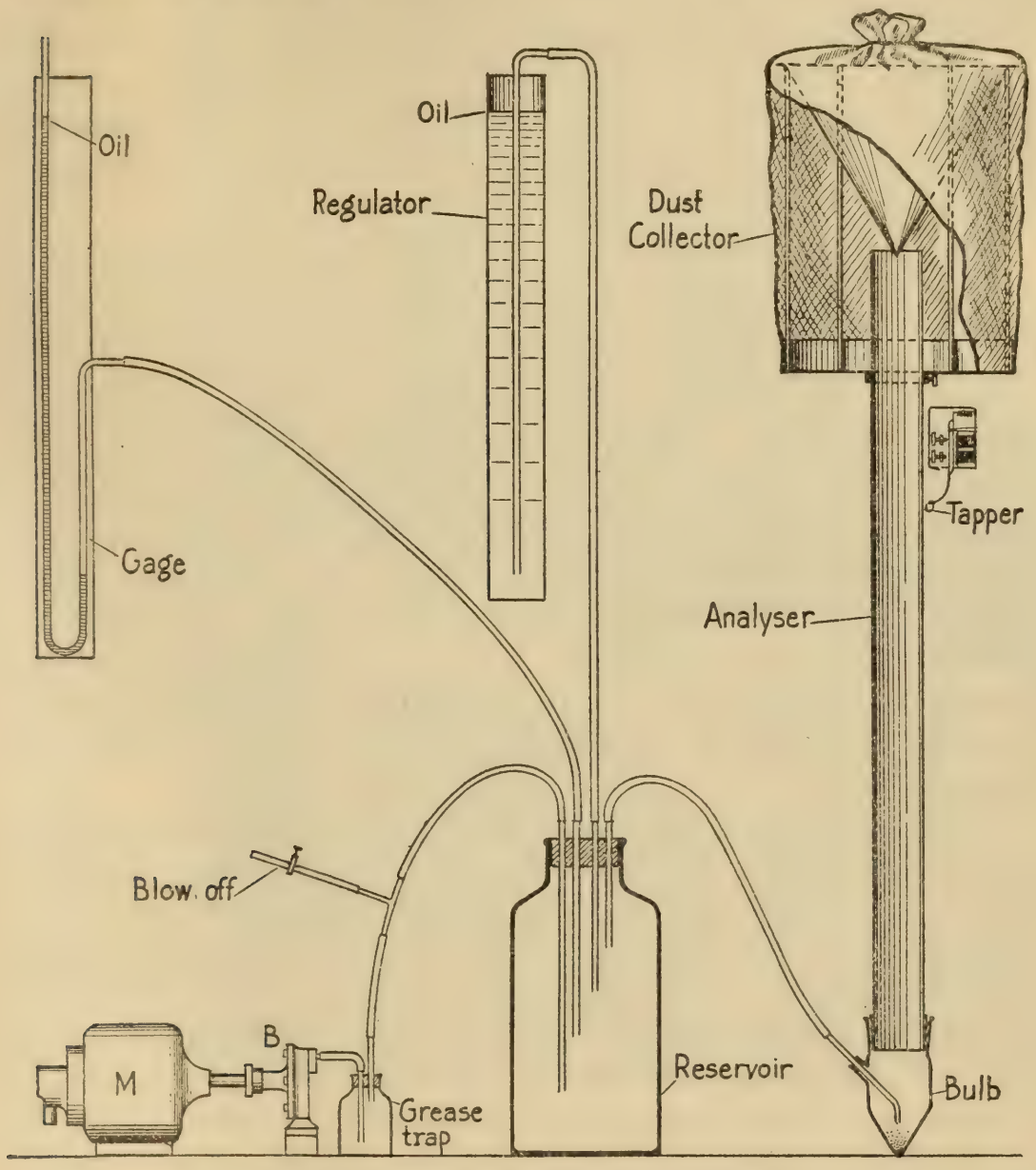

FIG. 17.—*Bureau of Standards air analyzer*

changeable nozzles; the stack, or separating chamber; the tapper, electrically operated; and the dust collector, which retains all material carried off through the separating chamber. The auxiliary apparatus required for the operation of the analyzer consists

of a motor *M*, direct connected to a blower *B*, beyond which is a grease trap to prevent oil and grease from getting into the air tube leading to the reservoir. A side valve is inserted in this tube which acts as a blow-off for the large excess of air delivered by the blower over and above the amount passing through the analyzer. The remainder of the air passes into a reservoir to which are connected an oil-pressure gage, a regulator, and finally the tube leading directly to the nozzle in the analyzer bulb. The auxiliary apparatus is designed entirely for the purpose of automatically supplying air at constant pressure to the analyzer.

It has been stated that a satisfactory elutriator should insure as far as possible a constant velocity and uniform stream lines in the fluid as it passes through the separating chamber. In our apparatus the separating chamber is a drawn brass tube 6.8 cm (2.7 inches) internal diameter, 7 cm external diameter, 150 cm (60 inches) long, polished on the inside without a projection of any sort on the inside walls. The air expands immediately after striking into the cement, and aside from the unavoidable pulsations and eddies in the bulb should have every opportunity to flow uniformly up the stack. Experiments will be described later which tend to show that the stack is sufficiently high to insure uniform stream lines and to indicate that the friction between the air stream and the polished surface of the stack has a negligible influence on the separations.

The second requirement of a satisfactory elutriator is that neither the cement nor the dust collector should retard the air delivery, unless such retardation be compensated in some way. This requirement is met particularly well by the distinguishing feature of the apparatus, viz, the delivery of the air into the cement from an overhead nozzle, and by the type of collector which is shown in Fig. 17. That any appreciable back pressure arising from the use of a fair sized flannel sack as dust collector did not exist was shown by attaching a small pressure gage to the top of the glass stack used with the original pear-shaped bulb. This gage can be seen at the top of the analyzer marked *B* in Fig. 18. Even with the maximum air delivery, this pressure did not amount to more than a millimeter of kerosene. That the air delivery from the nozzle

FIG. 18.—*Section of laboratory equipped for air analysis of cements.* A, *an early form of "up-blast" analyzer, now used for removing dust from samples of cement and other materials.* B, *the original apparatus of the "down-blast" type. Very fine separations can not be made with this analyzer owing to small diameter of stack. Calibration is also uncertain because of the difficulty of getting pure slides at the end of an analysis.* C, *improved form of analyzer, better adapted to fine separations on account of its larger stack.* D, *present form of analyzer designed to give three well-distributed separations (four fractions) of the portion of cement passing a No. 200 sieve. The shape of the bulb and the collector of this apparatus are the chief improvements over analyzer* C

just above the cement is inappreciably retarded by the latter was to be inferred from early attempts to observe how much pressure change in the reservoir might be produced by bringing the free-blowing nozzle up toward a flat plate in such way that the air stream from the nozzle impinged vertically on the plate. No appreciable change was observed with maximum air delivery until the nozzle had approached to within 1 cm of the plate. In the present form of apparatus the combined retarding effect of cement and dust collector was determined by metering the air delivery from the separate nozzles, first when blowing free into the atmosphere, and again when blowing into the analyzer under normal operating conditions. With the largest nozzle used, the observed difference in air delivery under the two conditions was less than 1 per cent, an amount which theoretically affects the size of separation by less than 0.5 per cent.

Another requirement of a satisfactory analyzer is that the cement shall be completely and continuously exposed to the action of the air, otherwise complete and clean separations will not be obtained. In this apparatus the action depends entirely upon the air stream from the overhead nozzle having sufficient energy to penetrate to the apex of the bulb. It is obvious, therefore, that the separation of the finest fraction, requiring the use of the smallest nozzle and the minimum air delivery, is the only one which needs careful attention, for if this separation can be made satisfactorily, the coarser separations, requiring greater air delivery, will certainly cause no trouble. The most important variables which may effect the proper penetration of the air stream to the bottom of the cement are (1) the pressure of air in the reservoir, (2) the diameter of the stack, (3) the diameter of the bulb, (4) the shape of the bulb, (5) the diameter of the nozzle, and (6) the quantity of cement. More or less attention has been devoted to all these items in the development of the analyzer, and we have found that the most feasible method of operation is to choose a stack of such diameter that three different separations—that is, four fractions—can be readily obtained in the cement passing a No. 200 sieve.

It will be shown later that the stack used in the present form of apparatus, 6.8 cm (2.7 inches) internal diameter, is probably quite near the most efficient size to use for these three separations.

The diameter of the stack practically determines the diameter of the bulb, for the latter is at best very slightly larger than the diameter of the stack, thus allowing the attachment of the bulb to the gently tapered collar at the bottom of the stack. The interior of the top of the bulb is ground to the same taper as the brass collar, but slightly larger, so that it may fit closely over a thin strip of soft leather glued to the outer surface of the collar. This provides a perfectly dust-tight connection between bulb and stack, at the same time reducing danger of breakage and facilitating removal of the bulb for weighing. The extreme height of the bulb as represented in Fig. 17 is 19 cm (7.5 inches), the apex being 14 cm (5.5 inches) below the bottom of the stack. It has also been found most feasible to operate the analyzer with a constant air pressure in the reservoir, which is automatically kept at 1 pound per square inch (0.07 kg per square centimeter) in our present series of experiments.

Our aim has been to procure the various separations desired by simply changing nozzles, a set of which are ground with the same taper and fit into the bulb in the manner shown in Fig. 17. These nozzles are all adjusted to point vertically downward into the apex of the bulb. The original tentative selection of nozzles was based on the sizes of separation desired, and as the average diameter of the largest particles passing the No. 200 sieve is approximately 0.004 inch (0.1 mm), it was suggested that 0.003 inch (0.075 mm), 0.002 inch (0.05 mm), and 0.001 inch (0.025 mm), would be desirable limiting sizes for the finer separations. While these are not the exact sizes of the separations now obtained, and, in fact, differ considerably from what may be regarded as the true sizes of separation, we are accustomed to refer to the three nozzles as the 0.001, the 0.002, and the 0.003 inch nozzles, respectively, and for convenience they will be thus designated hereafter, although it should be always remembered that these are not the true sizes.

Referring to the statement at the beginning of the second paragraph, on page 27, it is the 0.001-inch nozzle which alone may not deliver air with sufficient energy to insure the complete stirring and mixing of the residue in the bulb. It happens that the

0.001-inch nozzle in the present apparatus delivering air at 1 pound per square inch is just capable of handling a 50 g sample of cement, but this was not accomplished without a number of attempts to improve the form of the conical part of the bulb. The latter is now a true cone with a slightly rounded apex, and an angle of 63°. The depth of the cement may be reduced by using a smaller sample, or by flattening the cone of the bulb, and a cone of 70° would probably give even better results than the one now in use. In routine examinations we are accustomed to use 33⅓ g of cement for the 0.001-inch analysis, which gives practically the same results as the 50 g sample and in less time. With a given size of stack and a fixed definite pressure in the reservoir, the diameters of the nozzles are practically predetermined. As the analyzer is calibrated entirely from the separations, however, we have never measured the nozzles accurately, and it may be emphasized here that neither the sizes of the nozzles nor any other dimensions of the apparatus, nor even the working pressure, need to be specified or known with accuracy. As a matter of record, the internal diameters of the nozzles now in use are approximately 1.1 mm (0.04 inch), 2.2 mm (0.09 inch), and 3.3 mm (0.13 inch), respectively.

The fourth important requirement of a good analyzer is that it should have no places of lodgment for material in the separating chamber. This is an obvious requirement for sharp and complete separations, and means that whenever an analysis is interrupted for any reason, all the material should soon settle either in the dust collector or in the residue in the bottom of the analyzer. All possible precautions have been taken to insure complete separations in this apparatus, and the following features contribute especially to this end: (1) The stack is polished on the interior surface, but in spite of this a small amount of the finest dust will gradually collect in the upper part of the stack, and in a single analysis may amount to a few hundredths of a gram; (2) the upper rim of the stack is filed to a sharp knife-edge beveled outward and downward, so that any particles which might otherwise lodge on the rim are deposited in the collector; (3) an electrical tapper is mounted near the top of the stack, and is ordi-

narily kept running at the beginning of an analysis to assist in circulating the cement in the bulb, and at the end of an analysis to prevent all possible adherence of particles to the inside of the stack when the rates of loss are being determined; (4) the dust collector has been designed especially to prevent any material from falling back into the residue when it has once made the trip through the separating chamber.

The essential feature of the dust collector is a 60° cone of polished sheet copper, supported by eight rods soldered at regular intervals to the inside of the rim of the brass pan at the bottom, and so arranged that the apex of the cone projects slightly into the upper end of the stack. The effect of this device is to moderately accelerate the air stream as it leaves the stack without causing any appreciable retardation in the uniform air flow up the main part of the stack. At the same time the air stream is diverted symmetrically outward into the body of the collector without diminishing the vertical component of flow until the particles in suspension are safely carried beyond the region directly above the mouth of the stack. The frame of the collector carries a loose covering of canton flannel taped tightly around the pan and gathered at the top, thus providing an efficient filter for the more or less dust-laden air stream without causing an appreciable back pressure. In the center of the pan is fastened a brass sleeve which fits closely around the stack and insures the rigidity of the collector, and the whole is supported in its proper position by an adjustable clamp. The frame of the collector is approximately 25 cm (10 inches) in diameter and 50 cm (20 inches) high.

VI. METHOD OF OPERATION—SPECIMEN ANALYSES

The complete process of making a separation with the analyzer is carried out as follows:

The motor and blower are first started at slow speed, and the air tube leading from the reservoir to the analyzer is connected to the nozzle to be used. This causes a rise in pressure in the reservoir, indicated on the gage, which is to be raised to the work-

ing pressure of 1 pound per square inch. The pressure is further raised by gradually closing the blow-off, and if not high enough when the latter is completely closed, the blower speed is increased. It is desirable always to have an excess of air supplied by the blower, and to have the blow-off so adjusted as to allow a slightly greater quantity of air to pass into the reservoir than is required for the analyzer. Further regulation of pressure is automatically provided by the regulator, which consists of a vertical pipe about 5 feet (150 cm) long and 4 inches (10 cm) in diameter, closed at the bottom and nearly filled with kerosene. Into this a long glass tube connected to the reservoir and open at the lower end projects to a depth which can be adjusted and is approximately the same as the difference in level of the kerosene in the two arms of the gage at working pressure. This adjustment is always made by trial, and when the proper depth is attained, the regulator functions perfectly for an indefinite time without further attention.

It is obvious that if the pressure in the reservoir is below the required working pressure, air can escape from the reservoir only through the analyzer nozzle, but by further closing the blow-off the pressure rises and the kerosene is driven down the regulator tube until finally the seal is broken and air bubbles off. The pressure in the reservoir will thereafter remain sensibly constant, unless the speed of the blower varies considerably. In normal operation, therefore, the oil in the pressure gage mounts quickly to its prescribed height and remains there while the regulator disposes of the slight excess of air supplied to the reservoir. Unavoidable irregularities in the speed of the blower are thus automatically compensated and the gage indicates the constant pressure of the air supplied to the nozzle. Variations in the reservoir pressure as large as 1 per cent are rare, and of this magnitude are entirely negligible in their effect on the separations.

Having adjusted the blow-off, as previously described, the nozzle is removed from the air tube and inserted in the bulb, which is detached from the stack. The weight of nozzle and bulb should be known to the nearest 0.01 g. If the 0.001-inch separation is to be made, a 33⅓ g sample of cement is placed in the bulb; if the coarser separations are desired, 50 g are ordina-

rily used. The bulb containing the cement is then attached to the stack, the air tube is connected to the nozzle, the tapper is started, and the analysis proceeds without further attention on the part of the operator. The residue in the bulb gradually darkens as the fine material is removed and in the course of half an hour or less appears to become distinctly granular, especially in the coarser separations. It has been found by experiment that greater uniformity in the fractions is obtained if the separations are regarded as completed when a certain rate of loss is reached, as in the case of the No. 200 sieve fineness determination. The air separations require a considerably longer time, however, as the diminution of the quantity of material removed is much less rapid toward the end of the process than in the sieve separations. The rate of progress of the air analyses is shown in Fig. 19.

We have arbitrarily adopted a loss of 0.02 g per minute as the most suitable rate to indicate the completion of a separation, but should the analyzer be found adapted to routine work, a considerable saving of time might be effected without much sacrifice of accuracy by adopting a higher rate. The rate of loss is determined in the following manner: The approximate time of an analysis is usually known from experience, and 15 or 20 minutes before the estimated time of completion the air tube is detached from the nozzle, and a half minute or more, depending upon the size of separation, is allowed for the particles suspended in the stack to settle back into the bulb. The latter is then removed and weighed. It is then replaced on the stack and the analysis is continued for exactly 10 minutes, after which the bulb and residue are again weighed. If the observed loss is greater than 0.2 g, the analysis is continued for another 10 minutes, and so on until a loss of 0.2 g or less has been observed in the 10-minute interval. The analysis is then completed, and the total loss computed to the minute when approximately 0.02 g was being removed. The total loss is expressed in percentage of the total cement, and check tests usually show an agreement within 0.5 per cent.

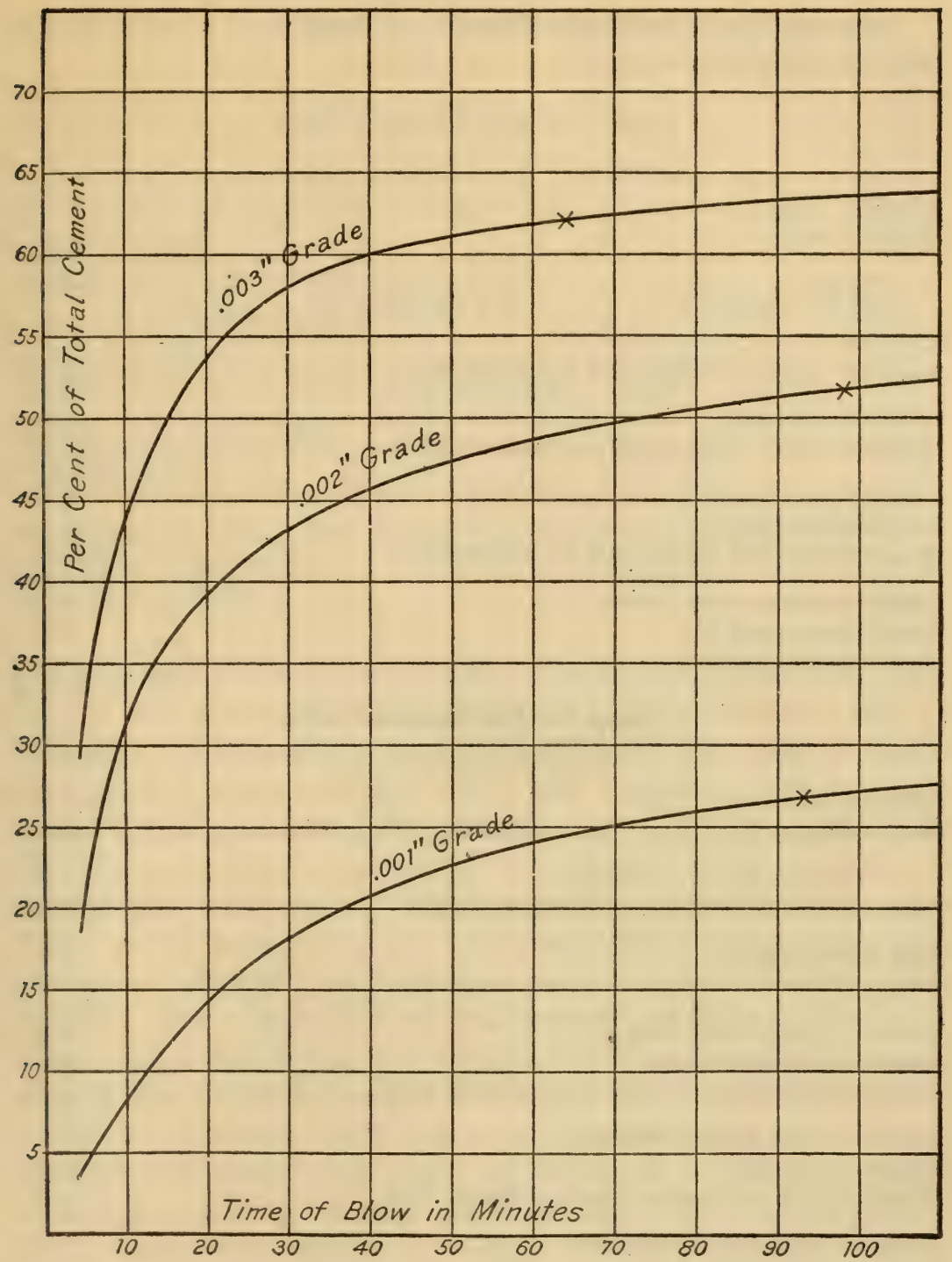

FIG. 19.—*Curves showing rate of removal of fine material in air analyses; 33⅓-gram samples used. The cement from which these curves were obtained is peculiar in having an unusually low "flour" content (0.001-inch grade) in comparison with the quantities of the coarser grades, 81 per cent passing the No. 200 sieve. The end points of the analyses are indicated by crosses*

Three specimen analyses, exactly as made and entered in our records, are given below:

Cement No. 406,[a] 0.001-inch nozzle

[Monday, Dec. 7, 1914, began at 4.17 p. m.]

Weight of bulb	251. 10 g
Weight of cement	33. 33
Total	284. 43
(Analysis interrupted at 4.43 p. m. and continued Dec. 8, beginning at 8.58 a. m.)	
Weight of bulb and residue after 80 minutes blow	274. 67
Loss in 80 minutes	9. 76
Weight of bulb and residue after 90 minutes blow	274. 44
Loss from 80th to 90th minute	0. 23
Loss in 90 minutes	9. 99
Weight of bulb and residue after 100 minutes blow	274. 27
Loss from 90th to 100th minute	0. 17
Rate of loss in 90th min	0. 02
Total loss in 90 minutes	9. 99 g
	= 29. 97%

Cement No. 406, 0.002-inch nozzle

[Dec. 8, 1914, began 11.22 a. m.]

Weight of bulb	251. 10
Weight of cement	50. 00
Total	301. 10
Weight of bulb and residue after 90 minutes blow	276. 44
Loss in 90 minutes	24. 66
Weight of bulb and residue after 100 minutes blow	276. 18
Loss from 90th to 100th minute	0. 26
Loss in 100 minutes	24. 92
Weight of bulb and residue after 110 minutes blow	275. 95
Loss from 100th to 110th minute	0. 23
Loss in 110 minutes	25. 15
Weight of bulb and residue after 120 minutes blow	275. 77
Loss from 110th to 120th minute	0. 18
Rate of loss in 111th minute	0. 02
Total loss in 111 minutes	25. 17
	= 50. 34%

[a] Cement No. 406 is one of the standard samples furnished by the Bureau for tests of No. 200 sieves.

Cement No. 406, 0.003-inch nozzle

[Dec. 9, 1914, began 10.30 a. m.]

Weight of bulb	251.55 g
Weight of cement	50.00
Total	301.55
Weight of bulb and residue after 70 minutes blow	272.83
Loss in 70 minutes	28.72
Weight of bulb and residue after 80 minutes blow	272.60
Loss from 70th to 80th minute	0.23
Loss in 80 minutes	28.95
Weight of bulb and residue after 90 minutes blow	272.40
Loss from 80th to 90th minute	0.20
Loss in 90 minutes	29.15
Weight of bulb and residue after 100 minutes blow	272.23
Loss from 90th to 100th minute	0.17
Rate of loss in 85th minute	0.02
Total loss in 85 minutes	29.05
	= 58.10%

The actual records are of course in more condensed form, each step in the above analyses being fully indicated for the sake of clearness. The operator also carefully notes the time of beginning each 10-minute check test. The stopping point is determined by simple linear interpolation of rates and is approximate only, but quite close enough for all practical purposes. This is carried out as follows for the 0.003-inch separation: 0.023 g is taken as the rate of loss at the seventy-fifth minute, 0.020 g as the rate at the eighty-fifth minute, and 0.017 g at the ninety-fifth minute. The eighty-fifth minute is therefore taken as the stopping point. The loss in 80 minutes was 28.95 g, and the rate of loss at the eightieth minute was assumed to be the mean rate between the seventy-fifth and eighty-fifth minutes, or 0.0215 g. Similarly the mean rate from the eightieth to the eighty-fifth minute is 0.0208 g and the loss from the eightieth to the eighty-fifth minute is 5×0.0208, or 0.10 g. Hence the total loss in 85 minutes is 29.05 g. While this procedure illustrates every step of the process, a simple inspection is generally all that is necessary to determine both the stopping point and the total loss.

The foregoing separations, combined with the fineness as determined on the No. 100 and No. 200 sieves, give a division of the

cement into six fractions. These fractions can be compared with similar fractions of other cements obtained in the same way, and thus interesting information can be obtained regarding the performance of different finishing mills, the increase in the finer grades by regrinding, and the relation between the amount of the 0.001-inch grade, which may be provisionally called "flour," and the amount passing the No. 200 sieve, which is the present method of judging the fineness of different cements.

VII. CALIBRATION OF THE ANALYZER—METHODS OF MEASURING PARTICLES

The quantitative separation of cement into fractions, as described in the preceding section, constitutes an analysis which can be interpreted only with reference to the particular apparatus employed and is not an absolute mechanical analysis. The very great desirability of obtaining comparable analyses of a given cement from different analyzers is in itself sufficient justification for earnest efforts to interpret the separations in terms of size of particles, and if this can be accomplished with even a fair degree of success it carries with it many practical advantages. For example, if we are assured that an analyzer is correct in principle both as to construction and operation, the determination of its sizes of separation does away with the necessity of knowing or referring in any way to its dimensions or to the details of operation; and the laborious adjustment of many parts, which must otherwise be carefully constructed and tested for the purpose of obtaining reliable comparisons, can be entirely avoided. On the other hand, the microscopic study of particles shows that the sizes of separation are not entirely dependent on the analyzer but depend also upon the peculiarities of the cements and possibly other conditions. Thus our problem is to determine first the nominal sizes of separation and then to establish in so far as possible the influence of various factors or conditions on the separations. The study of the latter part of the problem is a long investigation in itself and is logically preceded by a discussion of the methods of measuring particles and a selection of some working method which may be either regarded as a standard system of measurement or reducible to a standard system. The method of

calibrating the analyzer which we have provisionally adopted is entirely covered in the following discussion of methods of measuring particles.

Ambiguity arises from the fact that cement particles are not spheres but irregularly shaped fragments resembling lumps of coal or unground cement clinker. The true sizes—that is, the volumes—of particles can therefore only be approximately determined, and the most feasible method appears to be the averaging of a large number of microscopic measurements of individual particles. As a rule the length, breadth, and thickness of particles as seen on a microscopic slide are fairly definite dimensions which can be measured, and we have to assume, as in the case of larger particles, that the best approximation to volume is obtained by regarding the particles as ellipsoids whose axes are these dimensions. We then have as the volume of the particle

$$V = \frac{\pi}{6} L \times B \times T$$

where L, B, and T are the observed length, breadth, and thickness. The volume of an equivalent sphere is given by the expression

$$V = \frac{\pi}{6} D^3$$

where D is the diameter; and from these two relations

$$D = \sqrt[3]{L \times B \times T}$$

in which D is taken as the true mean diameter of the particle. But the measurement of three dimensions of fine particles is too laborious for routine calibrations, and it is desirable to find out whether some simpler system of measurement can not be adopted from which the true sizes may be deduced with considerable accuracy.

In our study of this phase of the problem measurements have been made on several thousand particles by different methods, but not all the sets are directly comparable and additional work needs to be done. Before making such comparisons as are possible the method of taking the slides should be described. When a separation has been completed, as described on page 32, the collector sack is opened at the top and pushed down over the

frame, exposing the open end of the stack. An elliptical piece of cardboard is then inserted obliquely into the top of the stack in such manner as to deflect the air stream almost entirely to one side of the copper cone. The bulb and residue are then replaced and the blow continued for several minutes. In order to obtain slides of the desired purity it is essential that all dust be first allowed to settle in the vicinity of the collector and that the analyzer be secure from the slightest jar. The slide is then held horizontally just outside and below the rim of the stack on the side to which the air stream is deflected by the card. From one to three minutes are usually required to obtain a slide having the desired number of particles.

The method of measurement originally adopted by us, and the method by which most of our measurements have been taken, was one which first seemed capable of giving the greatest uniformity, although it does not represent even approximately the true size of separation. In this method the diameters of the largest particles are measured—that is, the particles which appear to be largest—irrespective of their orientation. In all our measurements a Bausch and Lomb petrographic microscope, with filar micrometer eyepiece and mechanical stage attachment, has been used. In measuring the particle diameters, which are always taken in the direction of travel of the movable cross hair, the latter is brought tangent first to one edge and then to the other, changing the focus when necessary to obtain sharp settings. The difference between the readings of the micrometer head in the two positions, multiplied by the value of the divisions in inches or millimeters, is taken as the diameter of the particle.

This system of measurement was followed for more than two years, for we believed that it not only afforded the greatest uniformity but also indicated the extreme limiting sizes of any given separation. We have recently discarded this system, however, after a series of comparisons with other methods, in favor of an average measurement of all the particles on a given slide. In the latter system an observer starts, let us say, at one corner of a slide, noting the readings of the two verniers on the mechanical stage. He measures the particle which is intersected by the fixed cross hair nearest the center of the field and then moves across

the slide measuring particles every 2 or 3 mm in a similar manner. The slide is then moved along a certain distance, depending upon the total number of measurements desired, and another line of particles across the slide is measured. In this manner the entire slide is covered and an average diameter of the particles is obtained from a purely mechanical selection.

TABLE 1

Uniformity of Results in Measuring Maximum Particles and Average Particles

Cement	Grade	Diameter of maximum particles by 3 observers				Diameter of average particles by 3 observers			
		P	S	G	Range	P	S	G	Range
		Inch	Inch	Inch	Inch	Inch	Inch	Inch	Inch
406	100 mesh	0.00929	0.00893	0.00860	0.00069	0.00786	0.00812	0.00781	0.00031
406	200 mesh	.00528	.00510	.00485	.00043	.00414	.00439	.00430	.00025
3008	0.003 inch	.00286	.00296	.00307	.00021	.00221	.00235	.00227	.00014
3296	do	282	280	268	14	201	210	193	17
3296	do	292	280	289	12	208	234	213	26
3457	do	280	264	270	16	209	216	199	17
3457	do	269	289	298	29	216	215	213	3
3693	do	309	287	291	22	222	222	224	2
3693	do	303	284	304	20	216	221	223	7
406	do	270	268	277	9	212	203	211	9
406	do	268	268	276	8	217	226	225	9
Mean		.00284	.00280	.00287	.00017	.00214	.00220	.00214	.00012
3008	0.002 inch	.00203	.00199	.00206	.00007	.00150	.00139	.00148	.00011
3008	do	207	203	213	10	150	166	159	16
3296	do	204	204	199	5	143	164	145	21
3296	do	202	202	199	3	155	168	158	13
3457	do	188	192	198	10	143	147	141	6
3457	do	196	200	209	13	150	161	156	11
3693	do	210	218	200	18	165	164	157	8
3693	do	214	207	220	13	168	163	161	7
406	do	190	182	187	8	142	152	151	10
406	do	184	180	183	4	150	152	148	4
Mean		.00200	.00199	.00201	.00009	.00152	.00158	.00152	.00011
3008	0.001 inch	.00098	.00112	.00102	.00014	.00079	.00078	.00076	.00003
3296	do	101	106	98	8	74	80	73	7
3457	do	93	103	91	12	74	70	68	6
3457	do	96	92	98	6	77	74	76	3
3693	do	104	100	98	6	74	75	79	5
3693	do	105	107	109	4	76	78	80	4
406	do	102	98	98	4	76	81	77	5
406	do	94	98	100	6	72	80	72	8
Mean		.00099	.00102	.00099	.00008	.00075	.00077	.00075	.00005

Table 1 contains all comparable sets of measurements made by the two methods described in the foregoing paragraphs. In general, each line of the table contains measurements by three observers on a single slide, but in a few cases on two similar slides. Columns 1 and 2 contain the laboratory numbers and the nominal sizes of separation of the cements used; columns 3, 4, 5, 7, 8, and 9 contain the individual measurements by three observers, each recorded value being the average diameter of 40 particles; and columns 6 and 10 show the ranges of the three observers' determinations in the two methods of measurement.

It is to be noted that from the average ranges for each grade that in all cases except one the selection of average particles gives more uniform results than the selection of the largest particles. It was anticipated also that in the selection of the largest particles personal differences would be more apt to appear than in the mechanical selection of average particles. In our earlier measurements this was undoubtedly the case, but the three observers responsible for the measurements herein reported show little variation in the selection of maximum particles, whereas observer S shows slightly higher values throughout in the selection of average particles. The only explanation that may be offered to account for this discrepancy is that the observer had had no previous experience in microscopic measurements and in the earlier part of the work had not understood that the focus should be changed, if necessary, in the two settings on each particle. This probably resulted in slightly larger diameters, and may account for the peculiarity noted. Certainly only very slight personal differences should be looked for in the selection of average particles, as indicated by the agreement of the average measurements of observers P and G.

There are also further objections to the selection of maximum particles for measurement, one of the most obvious being the failure of this system to indicate the true size of separation. It has also been observed, as might be anticipated, that larger diameters are obtained from slides thickly covered with particles than from thin slides, and low magnifications tend to yield higher results than high magnifications, because of the larger field of the former.

But the main objection to this system has been brought out by three dimensional measurements, which establish quite conclusively that the majority of the apparently largest particles as seen in a plane are usually lamellar in form and do not vary so greatly from the true average size as their appearance would indicate. This is shown by the comparison of results presented in Tables 3 and 4. On the other hand, the selection of particles at random—that is, the average selection as described on page 38 is made without the mental effort required in the other system. It represents more nearly the actual size of separation, and can be reduced to the true size if desired with a fair degree of approximation. It does require, however, representative slides of great purity, in the making of which every precaution must be taken to avoid contamination.

Table 2 is prepared from the same data as Table 1, but contains, in place of the individual observers' measurements, the averages of all. Each recorded diameter is therefore an average of measurements on 120 particles. The last column shows the relation between the diameters of particles of the same grades as determined by the two systems of measurement, an average value of the ratio, average diameter to maximum diameter, being derived for each grade. These average values for the 0.001-inch, 0.002-inch, and 0.003-inch grades—that is, for the air separated grades—are in very good agreement, and we may assume the value 0.765 as a very approximate reduction factor from the older system of measurement to the present system. As previously stated, the sieve separations are more strictly on a basis of absolute size than the air separations, consequently less difference between maximum and average sizes are to be expected, and the reduction factors are therefore higher. Furthermore, the No. 200 sieves are relatively much less uniform than the No. 100 sieves, and the reduction factor for the 100-mesh grade is therefore higher than that for the 200-mesh grade.

The three dimensional measurements have thus far been made by one observer, but it is highly desirable that the accuracy and uniformity of such measurements be checked by others. We hope that this phase of the investigation may be further extended, for

the information to be obtained from these studies has a very important bearing on the theory of elutriation as well as on the

TABLE 2

Relation Between the Diameters of Maximum Particles and Average Particles

Cement	Grade	Diameters of maximum particles	Diameters of average particles	Ratio, average diameter to maximum diameter
		Inch	Inch	
406	100 mesh	0.00894	0.00793	0.887
406	200 mesh	.00508	.00428	.842
3008	0.003 inch	.00296	.00228	.771
3296	do	277	201	.726
3296	do	287	218	.759
3457	do	271	208	.768
3457	do	285	215	.755
3693	do	296	223	.754
3693	do	297	220	.741
406	do	272	209	.769
406	do	271	223	.824
Mean		.00283	.00216	.763
3008	0.002 inch	.00203	.00146	.720
3008	do	208	158	.760
3296	do	202	151	.748
3296	do	201	160	.796
3457	do	193	144	.747
3457	do	202	156	.773
3693	do	209	162	.776
3693	do	214	164	.767
406	do	186	148	.796
406	do	182	150	.825
Mean		.00200	.00154	.771
3008	0.001 inch	.00104	.00078	.750
3296	do	102	76	.745
3457	do	96	71	.740
3457	do	95	76	.800
3693	do	101	76	.752
3693	do	107	78	.729
406	do	99	78	.788
406	do	97	75	.773
Mean		.00100	.00076	.760

practical limits of the air analyzer. The measurement of the length, breadth, and thickness of a particle is now made as follows: For the length and breadth measurements the ordinary illumina-

tion from below the slide is used. Our mechanical stage does not revolve, therefore in order to bring the horizontal wire of the micrometer eyepiece parallel to the length of the particle the eyepiece is turned and the length is then measured in the usual manner. The eyepiece is then turned through 90°, approximately, and the tangent positions of the cross hair determine the breadth. In order to measure the thickness a strong side illumination is required, this being provided by an ordinary 40-watt tungsten lamp and a lens which concentrates the light on the particles directly beneath the microscope objective.

For best results the lamp is placed slightly above the level of the objective, in order that the highest points of the particles may be strongly illuminated. The microscope is first focused as closely as possible on the top surface of the glass slide and then upon the highest point of the particle, the difference in the readings of the micrometer head of the focusing screw in the two positions giving the thickness of the particle. This measurement of thickness is of course subject to relatively large error, especially on the very fine particles. Assuming the pitch of the focusing screw to be 0.25 mm (0.01 inch), the thickness of the 0.001-inch particles is such as to require only about one-twentieth of a turn of the screw to pass from the bottom to the top of the average particle. Nevertheless, if the observations are free from systematic error, the mean of a large number should give a fairly dependable result, the approximate accuracy of which can generally be checked by indirect methods. In these measurements we are practically limited to the use of an 8 mm objective, for the working distance of our 4 mm objective is too small to allow the particles to be illuminated from the side, and the 16 mm objective has been found to give too high values, owing to the relatively slow change in focus. A high-power objective with long working distance would therefore improve the thickness determinations, especially of the finer grades.

Tables 3 and 4 contain practically all results of observations that have been made to determine the length, breadth, and thickness of particles. The tables are arranged in the same manner as Tables 1 and 2, each line representing, except in a few cases, the average length, breadth, and thickness of 50 particles of a single

slide. It should be stated that the values in the sixth columns, $\sqrt[3]{L \times B \times T}$—that is, the true diameters—have been computed once for all from the mean values of L, B, and T, and are not the means of $\sqrt[3]{L \times B \times T}$ for each particle separately. This short cut has eliminated a vast amount of computation, and the

TABLE 3

Summary of Three Dimensional Measurements on Maximum Particles

Cement	Grade	L	B	T	$\sqrt[3]{L \times B \times T}$	Objective	Remarks
		'Inch	Inch	Inch	Inch		
406	100 mesh	0.00946	0.00770	0.00534	0.00730	16	Sieve 631.
406	do	983	769	534	739	16	Do.
Mean		.00964	.00770	.00534	.00734		
406	200 mesh	.00534	.00425	.00235	.00376	16	Sieve 576.
406	do	527	416	236	373	16	Do.
421	do	564	440	224	381	16	Do.
421	do	552	445	231	384	16	Do.
Mean		.00544	.00432	.00232	.00378		
406	0.003 inch	.00309	.00251	.00107	.00202	16	7-foot stack.
406	do	303	252	102	198	16	Do.
406	do	292	240	94	187	16	6-foot stack.
406	do	303	246	98	194	16	Do.
Mean		.00302	.00247	[a].00100	[a].00195		
406	0.002 inch	.00214	.00163	.00062	.00130	8	8-foot stack.
406	do	201	161	63	127	8	Do.
406	do	200	171	72	135	8	7-foot stack.
406	do	194	165	75	134	8	6-foot stack.
Mean		.00202	.00165	.00068	.00132		
406	0.001 inch	.00107	.00084	.00039	.00071	8	7-foot stack.
406	do	103	82	34	66	8	Do.
406	do	107	84	36	69	8	6-foot stack.
406	do	107	84	34	67	8	Do.
Mean		.00106	.00084	.00036	.00068		

[a] These readings are questionable, see text, pp. 44–46.

values given probably differ by a negligible amount from those obtained by the longer method. It will be noted that all observations on air-separated particles made with the 16 mm objective are regarded as questionable, the thickness measurements being undoubtedly too high. This is indicated in Table 4 by the com-

parison of thickness measurements in the 0.003-inch and 0.002-inch grades, where it is observed that the low magnifications give higher values.

TABLE 4

Summary of Three Dimensional Measurements on Average Particles

Cement	Grade	L	B	T	$\sqrt[3]{L \times B \times T}$	Objective	Remarks
		Inch	Inch	Inch	Inch		
406	100 mesh	0.00845	0.00703	0.00553	0.00690	16	Sieve 631.
406	200 mesh	.00466	.00368	.00298	.00371	16	Sieve 576.
406	0.003 inch	.00242	.00176	[a].00178	[a].00197	16	5-foot stack.
406	do	231	176	137	177	8	Do.
3457	do	235	173	[a]191	[a]198	16	Do.
3457	do	245	183	133	181	8	Do.
3008	do	240	176	137	180	8	Do.
3693	do	233	188	125	176	8	Do.
Mean		.00237	.00181	.00133	.00178		
406	0.002 inch	.00164	.00123	.00108	.00129	8	Do.
3457	do	177	136	[a]125	[a]144	16	Do.
3457	do	168	127	90	124	8	Do.
3008	do	172	134	98	131	8	Do.
3693	do	174	135	95	131	8	Do.
Mean		.00170	.00130	.00098	.00129		
406	0.001 inch	.00086	.00063	.00056	.00067	8	Do.
3457	do	82	59	47	61	8	Do.
3008	do	90	64	52	67	8	Do.
3693	do	90	64	59	70	8	Do.
Mean		.00087	.00062	.00054	.00066		

[a] These readings are questionable and not included in means, see text, pp. 44–46.

The most striking result of comparisons of Tables 3 and 4 is brought out by tabulating the average true diameters of the different grades of all cements side by side as follows:

True Diameters ($\sqrt[3]{L \times B \times T}$)

Grade	Maximum particles	Average particles
	Inch	Inch
100 mesh	0.00734	0.00690
200 mesh	.00378	.00371
0.003 inch	.00195	.00178
0.002 inch	.00132	.00129
0.001 inch	.00068	.00066

The true diameters of the maximum particles are seen to differ but little, relatively, from the true diameters of the average particles, except in the 0.003-inch grade, where the maximum diameter appears to be considerably greater. All the measurements on the maximum particles of this grade, however, were made with the 16-mm objective, and the comparison therefore corroborates the more direct evidence from Table 4 that this objective gives too high values when used for thickness determinations. The same objection applies to the use of the 16-mm objective on the sieve grades, but here the relative error is of course smaller. The three dimensional measurements thus establish the fact that the apparent maximum particles are but little larger, on the average, than the average particles, from which we may infer that the apparent maximum particles are lamellar in form. In fact, many of these particles appear under ordinary observation to be comparatively thin, if one may judge of this by their relative translucency.

Hazen has stated [9] that in examinations of sand particles separated by elutriation methods, he found the true average diameter of such particles to be approximately the same as the shorter diameter as seen in a plane in the ordinary microscopic observations. It is interesting to note that this relation holds very closely between the average breadths and true diameters recorded in Table 4. This is more readily seen by the following tabulation:

Grade	Breadth	True diameter
	Inch	Inch
100 mesh	0.00703	0.00690
200 mesh	.00368	.00371
0.003 inch	.00181	.00178
0.002 inch	.00130	.00129
0.001 inch	.00062	.00066

The only discrepancy amounting to more than 1 or 2 per cent is in the 0.001-inch grade, which confirms, to some slight extent,

[9] Some Physical Properties of Sands and Gravels, Allen Hazen; Twenty-fourth Annual Report of Mass. Board of Health, 1892.

the suspicion that the 8-mm objective may be giving too high results on these very small particles, just as the 16-mm objective was giving too high values on the coarser grades. Nevertheless, the generally excellent agreement between these figures suggests the abbreviated method of simply measuring the breadths of average particles, a method which avoids the laborious measurements of thickness and yet gives the approximate true diameters. It is also interesting to note that liquid elutriations of sand particles can apparently be compared with air elutriations of cement particles on the basis of absolute size without reference to the apparatus used for making the determinations.

One other comparison of data from the preceding tables may be of interest. We should anticipate that the methods of measurement described on page 38 would yield apparent diameters which are approximately the mean of the lengths and breadths of the same or similar particles. The following tabulation of the mean values for the different grades enables this comparison to be made more readily:

Grade	Apparent maximum diameters (Table 2)	Mean of length and breadth, maximum particles (Table 3)	Apparent average diameters (Table 2)	Mean of length and breadth, average particles (Table 4)
	Inch	Inch	Inch	Inch
100 mesh	0.00894	0.00867	0.00793	0.00774
200 mesh	.00508	.00488	.00428	.00417
0.003 inch	.00283	.00274	.00216	.00209
0.002 inch	.00200	.00184	.00154	.00150
0.001 inch	.00100	.00095	.00076	.00074

These values show that if the apparent diameters of particles are measured on a microscopic slide in one direction without regard to the orientation of the particles, the results obtained will be very slightly larger than the mean of the length and breadth measured separately. In the case of particles selected at random this difference is of the order of 2 or 3 per cent.

TABLE 5

Relation of the Apparent Diameters and the True Diameters of Average Particles

Cement	Grade	Apparent diameters of average particles	True diameters of average particles	Ratio, true diameter to apparent diameter
		Inch	Inch	
406	100 mesh	0.00793	0.00690	0.870
406	200 mesh	.00428	.00371	.868
3008	0.003 inch	.00228	.00180	.789
3457	do	.00212	.00181	.854
3693	do	.00222	.00176	.794
406	do	.00216	.00177	.820
Mean		.00220	.00178	.814
3008	0.002 inch	.00152	.00131	.862
3457	do	.00150	.00124	.828
3693	do	.00163	.00131	.804
406	do	.00149	.00129	.866
Mean		.00154	.00129	.840
3008	0.001 inch	.00078	.00067	.859
3457	do	.00074	.00061	.825
3693	do	.00077	.00070	.909
406	do	.00076	.00067	.882
Mean		.00076	.00066	.869

Table 5 contains a retabulation of all the comparable data in Tables 2 and 4 relating to the average or random selection of particles for measurement. The last column of the table contains the ratios of the true diameters to the apparent diameters; that is, the reduction factors for the latter system to the former. It will be observed that the mean ratios for the air-separated grades show a fairly regular increase in the factor with diminishing size of particle. To what extent this is a true increase we are unable to state at the present time. It is conceivable that the very fine particles may have less tendency than the coarser particles to lie on a slide in their most stable positions, owing to possible electrical or other attractions, in which case we should expect to find less differences between the apparent and true diameters, and consequently a higher reduction factor for the smaller particles. This may also be shown by tabulating the relative proportions of

the mean values of the three dimensions of the air-separated grades in Table 4. Thus, we have—

Grade	L	B	T	Relative proportions of L, B, and T
	Inch	Inch	Inch	
0.003 inch	0.00237	0.00181	0.00133	1:0.764:0.561
0.002 inch	.00170	.00130	.00098	1:0.766:0.576
0.001 inch	.00087	.00062	.00054	1:0.713:0.621

These proportions are somewhat irregular, but they do indicate an increase in the proportionate thickness of the finer particles. On the other hand, there is undoubtedly a tendency to overestimate the thickness by a more or less definite amount, depending on the magnification, this amount being relatively greater for the smaller particles if the same magnification is used throughout, as it was in these observations. We are inclined to believe, therefore, that while there may be a real increase in the reduction factor for small particles, it is probably not as great as indicated by the results in Table 5, and the maximum value for the particles included in these measurements is probably not over 0.85.

Our experience has indicated that certain modifications of the method of measuring three dimensions of microscopic particles will considerably reduce the labor of such observations and probably give equally good results. For example, if measurements on 50 particles are desired to determine the true average diameter of the particles on a given slide, it will require considerably less time and energy on the part of the observer if he measures the length and breadth on one set of 50 particles and the thickness on another set of 50. This is not wholly a matter of convenience for the observer, for, in general, a lower magnification is better adapted for the length and breadth measurements than for the thickness measurements, which appear to require the highest magnification that can be used. For example, a particle of the 0.002-inch grade requires only a 16 mm objective (total magnification 125) for a sufficiently accurate measurement of length and breadth, but an 8 mm objective (total magnification 260), or preferably a 4 mm objective (total magnification 560), for the thickness determination.

We have also considered the use of a micrometer ocular ruled in 0.1 mm cross section for the length and breadth determinations, but have not yet had an opportunity to test its usefulness. It seems probable that this device, if found adapted to these measurements, will save considerable time in calibration work.

The comparisons given in Tables 2 and 5 show what large discrepancies may arise in arbitrary methods of measuring and expressing sizes of particles. The question to be decided, therefore, is whether it is more desirable to report the mechanical analyses obtained with the air analyzer in terms of the apparent sizes determined by routine measurements, or to report them in absolute sizes determined by three dimensional measurements, trusting in the reliability of a reduction factor to reduce apparent sizes to absolute sizes when the latter are not directly determined. Theoretically, we should deal with absolute sizes; practically it is much more convenient to determine relative sizes by a simple method of measurement, and if the same system be followed in all analyses, there should be no objection to reporting results exactly as obtained. Thus, in ordinary mechanical analyses of sand no attention is paid to absolute sizes of grains but the nominal sizes of the screen openings are taken as the sizes of separation. These nominal openings are always less than the absolute size of separation, partly because some screen openings, especially in the finer sieves, are always larger than the nominal opening, partly because the nominal size corresponds more nearly to the mean of the breadth and thickness of the largest particles than to the mean of length, breadth, and thickness. These two factors have the combined effect of making the nominal screen opening correspond very nearly to the average thickness; that is, the average smallest dimension of the particles representing the size of separation. This is shown by data in Table 4, in which the thickness of the 100-mesh and 200-mesh particles were determined as 0.00553 and 0.00298 inch, respectively, the nominal 100-mesh and 200-mesh openings being 0.0055 and 0.0029 inch, respectively. In the routine measurements of microscopic particles, however, the nominal sizes of separation are very approximately the mean of the length and breadth, and therefore greater than the absolute sizes. In general, these nominal sizes of the air-separated grades

are about as much greater than their true sizes as the true sizes of the screened particles are greater than their nominal sizes, so that if the sieve grades are to be represented together with the air-separated grades by a complete mechanical analysis curve the sizes of the sieve separations must be taken in the same manner as the air-separated grades and not on the customary basis of nominal screen opening.

Chiefly on account of the simplicity of the method of measurement described at the bottom of page 38 we have adopted this system for the present as the basis of our mechanical analysis curves for cement. On this basis the nominal sizes of separation for the present analyzer, as obtained from the mean values in Table 2, are—

Grade	Size of separation (Inch)
100 mesh	0.00793
200 mesh	.00428
0.003 inch	.00216
0.002 inch	.00154
0.001 inch	.00076

the cements from which these values were derived representing a considerable variation in physical characteristics. Comparatively few observations have been made on the sieve separations, and some further measurements should be made to establish these sizes with greater certainty, but the foregoing values are probably quite approximate. It should be noted that the calibrations on the different cements differ appreciably, though not greatly, from each other and that the nominal sizes given above are the mean values obtained from a large number of observations. For practically all normal cements the nominal sizes may be considered the actual sizes of separation; only in special investigations will it be necessary to calibrate the analyzer from measurements on the particular material under observation.

Fig. 20 shows a complete mechanical analysis of the portion of cement No. 406 passing the No. 200 sieve, which may be considered typical of normal cements. In this diagram the mechanical analysis curve is plotted in the usual manner, the abscissae representing the sizes of separation and the ordinates representing the cumulative percentage of total material below the corresponding size of separation. The curve is drawn from the results

obtained with three different analyzers, shown at *B*, *C*, and *D*, Fig. 18. Of these analyzers, *D* must be considered the standard. Analyzer *C* is also capable of good separations and fairly close calibration, but because of its larger stack only the 0.001-inch grades and the 0.002-inch grades were obtained with it. Analyzer *B*, the original glass apparatus, gives fairly good separations, but is not adapted to close calibration. Because of its narrow stack, analyzer *B* gives only the 0.002 inch and 0.003 inch separations.

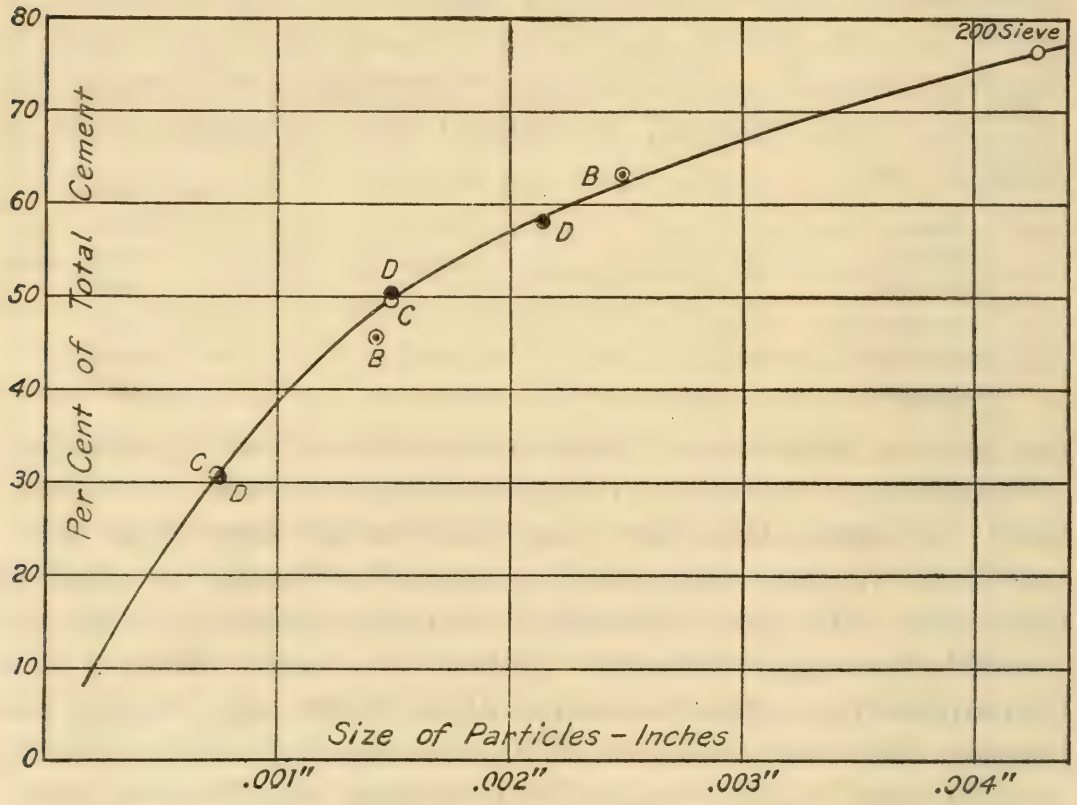

FIG. 20.—*Fineness curve of cement No. 406 as obtained from three analyzers, B, C, and D. (See Fig. 18)*

It is also observed that analyzer *D* would give a better distribution of its separations if the 0.003-inch nozzle were enlarged so as to increase the corresponding fraction by 5 or 6 per cent of the total cement. It is a mere coincidence that the sizes of separation of analyzers *C* and *D* are very close together, in consequence of which the fractions obtained with them are in very close agreement. The points obtained from analyzer *B* are subject to greater uncertainty, owing to the impossibility of obtain-

ing pure slides for calibration. The results of observations giving the data for the curve in Fig. 20 are recorded in Table 6.

TABLE 6

Data Obtained in the Mechanical Analysis of Cement No. 406, from Three Analyzers. (See Fig 18)

Analyzer	Grade	Diameters of average particles				Per cent of total cement
		P	S	G	Average diameter	
	Inch	Inch	Inch	Inch	Inch	
B	0.003	0.00233	0.00258	0.00256		63.10
B	.003	.00229	.00260	.00258		63.20
Mean	.....	.00231	.00259	.00257	0.00249	63.15
D	.003	.00212	.00203	.00211		58.30
D	.003	.00217	.00226	.00225		58.14
Mean	.....	.00214	.00214	.00218	.00215	58.22
B	.002	.00139	.00144	.00138		45.38
B	.002	.00148	.00139	.00149		45.76
Mean	.....	.00144	.00142	.00144	.00143	45.57
C	.002	.00138	.00140	.00144		49.78
C	.002	.00150	.00156	.00163		49.34
Mean	.....	.00144	.00148	.00154	.00149	49.56
D	.002	.00142	.00152	.00151		50.52
D	.002	.00150	.00152	.00148		50.22
Mean	.....	.00146	.00152	.00150	.00149	50.37
C	.001	.00073	.00076	.00073		30.72
C	.001	.00070	.00077	.00079		30.99
Mean	.....	.00072	.00076	.00076	.00075	30.86
D	.001	.00076	.00081	.00077		30.21
D	.001	.00072	.00080	.00072		30.66
Mean	.....	.00074	.00080	.00074	.00076	30.44

Summarizing, briefly, the results of these studies on particle measurements, we have shown that it is possible to calibrate the analyzer simply by determining its sizes of separation, without limiting in any way the dimensions or the operating conditions of the apparatus. The sizes of separation may be determined and

expressed in various ways, that which has been adopted being apparently the simplest and most direct, though not giving the true size as this term is ordinarily interpreted. Should it be found desirable to approximate quite closely the true sizes of separation, two methods of doing this, aside from actually making the three dimensional measurements, have been suggested—first, an approximate reduction factor has been determined by which the true sizes may be computed from the routine measurements; second, the mean true diameter of a set of particles representing the size of separation is very approximately the mean breadth of these particles, a measurement which can be made without difficulty, but less readily than the routine method of measuring diameters without regard to the orientation of the particles. It should finally be emphasized that the success of this routine method of calibration depends primarily on obtaining representative slides of the greatest possible purity, and the analyzer must be so constructed that pure slides can be readily obtained.

VIII. A STUDY OF CONDITIONS WHICH MAY INFLUENCE THE SEPARATIONS OF THE AIR ANALYZER

As stated in the preceding section, a critical study of the possible sources of error in air analysis of cements is a long investigation in itself, and up to the present time only the more obvious conditions which might affect the separations have been investigated. It is intended that the effects of these conditions and their relation to the theory of air elutriation shall be further studied.

The factors or conditions which are most likely to affect the air separations may be included in three groups—(1) those relating to the construction of the analyzer, (2) atmospheric conditions, (3) variations in the quantity and character of the cement. Under the first group will be considered the influence of the shape and dimensions of the apparatus and the effects of abrasion. The second group will include a discussion of external atmospheric conditions, variations in the working pressure, etc. The third group includes a great variety of conditions, comparatively few of which have been thus far investigated. This group is the most important and at the same time the most difficult to cover

thoroughly, and the results to be presented merely indicate what degree of reliability may be placed in the analyses when carried out under the assumption that all normal cements are subject to partition on the same basis.

1. CONDITIONS INVOLVED IN THE CONSTRUCTION OF THE ANALYZER

(*a*) SHAPE OF BULB, DIAMETERS OF NOZZLES, ETC.—Variations in these parts of the apparatus have already been discussed on pages 27–29. So far as we may judge from experience, these items do not affect the separations, provided their arrangement permits the air stream to have continued or intermittent access to the entire sample of cement. Practically, the shape of the bulb does have an important relation to the amount of cement that can be handled with the minimum air stream, and indirectly, therefore, determines to some extent the minimum size of separation obtainable with a given diameter of stack. The diameters of the nozzles do not need to be accurately determined or specified. It has been our custom to use three nozzles whose diameters are approximately in the ratio of 1:2:3, the smallest being so chosen that the size of its separation is somewhere near the limit of the "impalpable powder." From the dimensions and working pressure of our present apparatus it is possible to compute the approximate size of nozzle for any desired separation in any apparatus of this type.

(*b*) DIAMETER OF STACK.—It was stated on page 27 that the stack used in our present form of apparatus (6.8 cm internal diameter) is probably quite close to the most efficient size to use for three well-distributed separations in the portion of normal cement passing the No. 200 sieve. The reason for this lies in the fact that any particular analyzer of this type is better adapted to one particular size of separation than it is to either finer or coarser separations. Thus, in order to avoid unnecessary abrasion of the cement particles by the action of the air stream, the energy of the latter should be only great enough to insure the proper circulation of the cement. In a given apparatus with a given working pressure this determines the air delivery and consequently the velocity of air up the stack, which in turn determines the size of separation.

Greater air delivery gives a larger size of separation but more abrasion. Smaller air delivery will not handle the cement properly. Hence, we are obliged to design an analyzer which is best adapted to the smaller sizes of separation desired, at the same time permitting the desired range in sizes to be attained without excessive abrasion. In our apparatus the diameter of the stack is practically a minimum for the 0.001-inch grade, and as will be shown under the discussion of abrasion effects, nearly a maximum for the 0.003-inch grade.

(*c*) LENGTH OF STACK.—Since the separation of finely divided materials by elutriation methods depends on the "floating power" of the different particles, we should anticipate that the length of the analyzer stack beyond a certain minimum would not greatly affect the separations. However, it can hardly be presumed that particles just capable of suspension in a given air stream remain stationary. It is much more probable that toward the end of an analysis many particles are oscillating irregularly in all parts of the separating chamber. Consequently, if the air stream is retarded slightly by friction near the wall of the stack, the longer the latter, the more opportunity the particles might have to fall back, and we should therefore anticipate that a long stack would either give slightly smaller percentages than a short stack on a given separation or require a longer time for the completion of the analysis. It is also desirable to have the stack as short as possible for the sake of compactness and convenience in setting up. We therefore carried out a series of analyses in which all operating conditions were kept as constant as possible, but with diminishing lengths of stack. Our present form of analyzer was originally constructed as described in Section IV, except that the original length of the stack was 8 feet instead of 5 feet. Two complete analyses were made of the same carefully mixed cement with this stack, the length was then reduced to 7 feet, and two complete analyses of the cement were again made. This process was repeated on a 6-foot stack and finally on the 5-foot stack. The results of these analyses are given in Tables 7 and 8.

TABLE 7

Results of Observations Made to Determine Effect of Length of Analyzer Stack

Length of stack, in feet	Grade	Test No.	Average diameter of maximum particles	Per cent of total cement	Time of analysis
	Inch		Inch		Minutes
8	0.001	1	0.00092	29.46	101
8	.001	2	94	29.79	112
Mean			.00093	29.62	106
8	.002	1	.00187	50.88	140
8	.002	2	193	50.96	144
Mean			.00190	50.92	142
8	.003	1	.00285	59.90	90
8	.003	2	286	59.10	89
Mean			.00286	59.50	90
7	.001	1	.00094	29.61	111
7	.001	2	95	29.73	112
Mean			.00094	29.67	112
7	.002	1	.00188	50.42	140
7	.002	2	.00182	50.48	130
Mean			.00185	50.45	135
7	.003	1	.00282	59.10	113
7	.003	2	273	59.20	90
Mean			.00278	59.15	102
6	.001	1	.00098	29.88	97
6	.001	2	100	30.00	98
Mean			.00099	29.94	98
6	.002	1	.00186	50.94	130
6	.002	2	187	50.90	130
Mean			.00186	50.92	130
6	.003	1	.00267	59.00	101
6	.003	2	276	58.92	93
Mean			.00272	58.96	97
5	.001	1	.00095	30.21	95
5	.001	2	100	30.66	104
Mean			.00098	30.44	100

TABLE 7—Continued

Results of Observations Made to Determine Effects of Length of Analyzer Stack—Continued

Length of stack, in feet	Grade	Test No.	Average diameter of maximum particles	Per cent of total cement	Time of analysis
	Inch		Inch		Minutes
5	.002	1	.00181	50.52	116
5	.002	2	183	50.22	120
Mean			.00182	50.37	118
5	.003	1	.00272	58.30	90
5	.003	2	269	58.14	90
Mean			.00270	58.22	90

In Table 7 the individual results of the two independent analyses are given in order to show the general agreement of repeated separations and calibrations. All the results are given exactly as obtained, and it will be noted that in only one case do the separations fail to agree witihin a few tenths of 1 per cent. The calibrations were made according to the original system of measuring maximum particles and are in fair agreement. Each recorded diameter is the mean of 120 determinations, 40 by each of three observers.

TABLE 8

Summary of Results of Observations to Determine Effect of Length of Analyzer Stack

Length of stack in feet	0.001-inch grade			0.002-inch grade			0.003-inch grade		
	Size of particles	Per cent of total cement	Time of analysis	Size of particles	Per cent of total cement	Time of analysis	Size of particles	Per cent of total cement	Time of analysis
	Inch		Min.	Inch		Min.	Inch		Min.
8	0.00093	29.6	106	0.00190	50.9	142	0.00286	59.5	90
7	94	29.7	112	185	50.4	135	278	59.2	102
6	99	29.9	98	186	50.9	130	272	59.0	97
5	98	30.4	100	182	50.4	118	272	58.2	90

The summary in Table 8 enables us to draw the general conclusion that the length of the analyzer stack beyond a certain minimum does not greatly affect the mechanical analyses. There seems to be a tendency for the 0.001-inch particles to increase in

size with diminishing stack, but the percentage of this grade increases at the same time. On the other hand, the 0.003-inch particles appear to decrease in size with diminishing stack, the percentage of this grade also diminishing. The time required for separations are irregular and may depend more on atmospheric or other conditions than upon the length of stack. Possibly the analyses are completed a little sooner with the shorter lengths. It is intended later to continue this series beyond the minimum permissible length of stack. At present we are unable to account for the slight apparent changes, and are not convinced that further observations will confirm these changes.

(*d*) Abrasion Effects.—It will have been inferred from the description of the analyzer and its operation that the air delivery varies approximately as the square of the size of separation, and consequently the energy of the air stream varies in much the same manner. Now, the greater the energy of the air stream the greater the abrasion of the particles in the residue, and we are therefore interested in determining the actual effect of abrasion in the coarsest separation. We have attempted to determine the effects of abrasion in two ways—first, by blowing a sample with the 0.003-inch nozzle for many hours and noting the final rate of loss; second, by carrying an analysis through the successive grades on a single sample of cement, and comparing these results with analyses made in the usual way, in which fresh samples are used for each separation. The rates of loss during successive hours in the 0.003-inch separation of a 50 g sample of normal cement were as follows:

	Grams
Loss during third hour	0.76
Loss during fourth hour	.42
Loss during fifth hour	.23
Loss during sixth hour	.24
Loss during seventh hour	.22
Loss during eighth hour	.17
Loss during ninth hour	.15

From the ninth to eleventh hours the loss was sensibly constant, and we may assume the value of 0.15 g, or 0.3 per cent, as the loss per hour due to abrasion. In the second test described above, the first analysis was performed on fresh samples; the second was carried out by blowing the 0.001-inch residue

with the 0.002-inch nozzle, and finally the 0.002-inch residue with the 0.003-inch nozzle. The results obtained were as follows:

	0.001 inch	0.002 inch	0.003 inch
Per cent blown from fresh samples	30.84	51.10	58.56
Per cent blown from single sample	30.68	51.08	59.82

These results have been confirmed by other determinations. The total time required for the complete analysis on the single sample was six hours, indicating an average rate of loss of about 0.2 per cent per hour. This rate is, of course, lower than it would be for the 0.003-inch blow alone and roughly confirms that obtained by the other method. The actual time required for the 0.003-inch separation on a normal sample is about 1½ hours, and the maximum loss due to abrasion is therefore probably not greater than 0.5 per cent. For ordinary purposes this loss can be neglected, but allowance can be made for it if desired.

2. ATMOSPHERIC CONDITIONS

(*a*) Temperature and Barometric Conditions.—No certain effects on the separations due to variations in atmospheric pressure and temperature have thus far been detected, and if these have been at all appreciable their effects have been attributed to errors of observation. These conditions enter the problem only in their relation to the density and viscosity of the air, as the working pressure is maintained at a fixed point above atmospheric pressure, regardless of the actual barometric height. Theoretically, the density enters chiefly to alter the velocity of the air delivered by the nozzles, while the viscosity enters chiefly in the carrying power of the air. The maximum effect on the separations would probably be observed when the barometer was low and the thermometer high, but no observations have been made as yet for the definite purpose of establishing this relation.

(*b*) Humidity.—Comparative analyses with the air analyzer have been made under widely varying conditions of humidity, and the results have indicated that there is no necessity for the use of moisture absorbers in the air supply. In fact, if the air is very dry, or if close to the saturation point, the analyzer does not

function as well as it does under normal atmospheric conditions. In the former case there is a noticeable electrical effect in the bulb, the dust adhering strongly to the glass, and the analysis generally requiring a longer time. When the humidity is very high there is more sticking of the dust in the upper part of the stack. Neither of these conditions, however, interfere seriously with the working of the analyzer, nor do they appear to affect the results appreciably.

(*c*) VARIATIONS IN THE PRESSURE OF THE AIR SUPPLY.—Theoretically, the velocity of air from the nozzles varies as the square root of the pressure in the reservoir. For small variations in pressure, therefore, we should expect the corresponding variations in the air stream to be about one-half as great. But the size of separation varies approximately as the square root of the air velocity, hence we should anticipate that small changes in pressure in the reservoir would have a negligible effect on the separations. This has been confirmed experimentally by making comparative analyses at normal pressure, at 5 per cent below normal, and at 5 per cent above normal. The following percentages of "flour" were obtained from a normal cement under these conditions:

	Per cent.
Pressure 5 per cent above normal	30. 51
Pressure normal	29. 94
Pressure 5 per cent below normal	29. 67

These figures show that a difference of 10 per cent in pressure produced only about 1 per cent difference in the finest fraction. It is therefore quite safe to assume that small variations in pressure may be neglected in the operation of the analyzer.

(*d*) EDDY CURRENTS, IMPULSES, AND LACK OF UNIFORM VELOCITY IN THE STACK.—The observations recorded in Tables 7 and 8 furnish the only information available at the present time on possible effects arising from the general turbulence in the bulb and lower part of the separating chamber. It is presumed that pulses and eddy currents gradually disappear as the air stream rises in the separating chamber, and that the impulses imparted to coarse grains of the residue are not sufficient to carry excessively large particles into the collector. Friction of the air stream at the wall of the stack may conceivably produce a slightly higher velocity at the center, but the observations are not conclusive on this point.

3. VARIATIONS IN THE QUANTITY AND CHARACTER OF THE CEMENT

(*a*) SIZE OF SAMPLE—A number of comparable analyses have been made to determine whether the size of sample has any effect upon the apparent percentage value of the various fractions. Differences might be looked for in view of the arbitrary method of determining the stopping points, which in our work are indicated by a rate of loss of 0.02 g per minute for the standard 50 g sample. The following results were obtained with analyzers C and D (see Fig. 18):

Analyzer	Cement	Grade	Size of sample	Per cent of total cement	Time of analysis
		Inch	Grams		Minutes
D	x	0.001	50.00	30.54	151
D	x	.001	33.33	30.42	100
C	y	.001	50.00	34.72	110
C	y	.001	33.33	34.68	76
C	z	.001	50.00	30.90	95
C	z	.001	33.33	30.84	68
C	z	.001	25.00	30.72	55
C	z	.002	50.00	50.62	97
C	z	.002	25.00	50.80	57

The foregoing results indicate a very slight and negligible tendency to obtain higher percentages with the larger samples. The end points in all these analyses were determined by the same rate of loss, and the agreement was quite unexpected before these and similar observations demonstrated that for all practical purposes analyses of samples ranging from 25 to 50 g would give concordant results with exactly the same criterion for completion. It may be noted, however, that the time of the analysis is roughly proportional to the size of sample in a given analyzer, and for different samples the more finely ground material requires a longer time. If samples of the same size are used for the three separations in a given analyzer, the times decrease with increasing size of separation. For example, in analyzer D the complete 0.001-inch separation of a 50-g sample requires normally 150 minutes, the 0.002-inch separation about 120 minutes, and the 0.003-inch separation about 90 minutes. Below are given comparative results of "flour" determinations on small samples of

different sizes in a bulb formerly used with analyzer D but later broken.

Size of sample in grams	Per cent of total cement	Time of analysis
		Minutes
25.00	27.44	100
20.00	27.95	70
16.67	29.34	65
12.50	28.72	46
10.00	28.60	36
8.33	28.56	30

These results are in very fair agreement for the amounts used, the last three in particular agreeing much more closely than the conditions warrant. The variation in the first three analyses is more normal and, in general, the variation is greater for smaller samples.

(*b*) Specific Gravity.—The varying specific gravity is undoubtedly the most important item to be considered in relation to its effect on the analyzer separations. Theoretically, the size of separation varies inversely as the square root of the specific gravity, other conditions remaining unchanged; and as we must deal with a range of at least 10 per cent in the specific gravity of various sized particles, we may expect to find corresponding discrepancies of 5 per cent in the sizes of separation. The varied specific gravity of different cements and of the various sizes of particles of a nonhomogeneous material like cement is an absolutely unavoidable source of error in every elutriation process, but, if necessary, calibrations can be made in important cases, these calibrations requiring but little more time than the actual analyses as now carried out. Many observations on cements of different gravities will be required to establish with certainty the limitations of the analyzer in this respect; that is, to establish the probable range in sizes of separation of any one grade. At present the available data simply indicate what order of error may arise if this and other variables are not taken into account.

The cements from which the data of Tables 1 to 5 have been collected were chosen particularly because they represent a con-

siderable variation in physical characteristics. The pertinent characteristics of four of these cements and the results of the analyzer separations and calibrations are given in the following table:

TABLE 9

Results of Analyzer Separations and Calibrations on Cements of Different Specific Gravities

Cement	Grade	Original condition				After treatment			
		Specific gravity	Ignition loss	Size of separation	Per cent of total cement	Specific gravity	Ignition loss	Size of separation	Per cent of total cement
	Inch		Per ct.	Inch			Per ct.	Inch	
3008	0.001	3.00	5.54	0.00078	33.54	(?)[a]	0.46	0.00082	32.19
	.002			.00146	54.26			.00158	52.60
	.003			.00208	63.02			.00228	61.48
3296	.001	3.13	2.97	.00076	29.55	(?)[a]	0.26	.00078	27.24
	.002			.00151	47.48			.00160	46.32
	.003			.00201	55.46			.00218	54.42
3457	.001	3.24	0.62	.00071	28.80	3.22	1.22	.00076	28.26
	.002			.00144	47.90			.00156	47.96
	.003			.00208	56.94			.00215	56.62
3693	.001	3.12	2.12	.00076	28.74	3.10	3.04	.00078	27.93
	.002			.00162	46.74			.00164	45.78
	.003			.00223	54.30			.00220	53.84

[a] Unfortunately these samples were accidentally destroyed before the specific gravities were redetermined.

Cement No. 3008 has abnormally low gravity and high ignition loss, and fails to meet the ordinary specifications. It appears to be an old sample, or else to have been unduly exposed. Cement No. 3457 has high gravity and low loss, and appears to be fresh from the mill. Cements Nos. 3296 and 3693 are more nearly normal, the latter being ditinguished by certain peculiarities in manufacture. All the cements were tested in the analyzer in their original condition, and calibrations of the separations were made. Portions of Nos. 3008 and 3296 were ignited at about 900° C and again tested and calibrated. Portions of Nos. 3457 and 3693 were exposed to the atmosphere for about six weeks, during which time the average humidity was fairly high, and again tested and calibrated. The results of these retests are given in the last four columns of Table 9.

It was anticipated that the tests of the ignited samples would show lower percentages and smaller sizes of separation than the original samples, especially in the 0.001-inch grade. The percentages of the various fractions are seen to be lower, but the sizes of separation are apparently higher. This must be attributed to the blasted condition of the particles whose edges were so serrated after the heat treatment that accurate measurements could not be made under the microscope. It was also anticipated that the tests of the exposed samples would show higher percentages and larger sizes of separation than the original samples, especially in the 0.001-inch grade. The sizes of separation are seen to be slightly higher, but the percentages are generally lower. This must be attributed to the damp condition of the samples when retested, which probably prevented clean separations in the analyzer. We are not wholly satisfied with this explanation, however, for the 0.003-inch particles appear under the microscope to be only very slightly affected by either treatment. It would undoubtedly be safer at the present time to disregard the results on the treated samples, simply on the ground that all of them were tested in a condition not encountered in normal tests.

Referring to the original tests, it is to be noted that the sizes of separation of the 0.001-inch grade vary inversely as the average specific gravities. In general this is as it should be, for undoubtedly the large differences in gravity are to be attributed to the condition of the finest particles and not of the cement as a whole. Hence, no definite relation can be sought between the average specific gravity of a cement and the sizes of its coarser particles; in fact, the only proper method of studying this problem is to compare the true sizes of separation with the gravities of the separate fractions. Even this is likely to lead to error in the "flour" fraction, of which the average gravity may be appreciably less than that of the largest particles of the fraction. The labor of carrying out this investigation in the manner suggested is great, and perhaps it is better for the present to accept the theoretical effects of gravity as the actual effects than to try to establish them experimentally.

The figures in the fifth column of Table 9 show a range of 10 per cent or more in the corresponding sizes of separation.

In view of the fact that the cements chosen cover nearly the normal range of specific gravity we may assume that this 10 per cent range represents approximately the limits of uncertainty in the size of separation with a given nozzle. This means that the sizes of separation may vary in extreme cases about 5 per cent from the nominal sizes, and by referring to the typical fineness curve in Fig. 20 it is possible to determine what error may be expected in estimating the percentage of any given fraction from its size of separation. If one does this on a carefully plotted curve, he will find that an error of 5 per cent in the size of separation yields an uncertainty of less than 1.5 per cent in the corresponding fraction, expressed as per cent of total cement.

(*c*) AGING.—The effects of aging on the physical properties of cement are presumably the lowering of the specific gravity by absorption of water and carbon dioxide, and an increase in fineness due to possible decrepitation of coarser particles. No tests have been undertaken with the air analyzer to establish these changes directly on given samples of cement, but it is quite certain that the finer fractions especially will show a small increase on account of the gradual changes in gravity.

It has been generally assumed that cements increase in fineness with age, but in certain cases we have established beyond question that cements may decrease in fineness, as indicated by very careful No. 200-sieve tests. This phenomenon can be explained on the assumption of a gradually developing adhesion of very fine material to the coarser particles, sufficient to more than offset any decrepitation that may have taken place. We believe the air analyzer is capable of giving more definite information on this subject, and a series of analyses will be undertaken for this purpose.

(*d*) SHAPE OF PARTICLES.—It has been suggested that the shapes of fine particles might distinguish cements ground in different types of finishing mills, and might possibly have some influence on the air separations. In our earlier microscopic measurements no particular attention was given to this matter, and if there were characteristic differences in the appearance of certain cements they were not sufficiently striking to suggest more careful examination. Recently a number of cements from different mills have been examined with a view to identification simply by the appearance of the

particles as obtained for calibration of the analyzer. These cements were as follows: No. 946, a tube-mill product; No. 1149, tube mill with cyl-peb compartments; No. 1150, tube mill exclusively with steel slugs; No. 2079, a Fuller-Lehigh product; No. 2387, crushed between rolls and air separated; No. 3296, wet-process cement, grinder unknown.

Slides were prepared representing the three sizes of separation of each cement, 18 in all. These were examined individually by three observers, and notes were made of any peculiarities. Some days later attempts to identify the cements were made by each observer, judging solely from the notes he had previously made. In 18 trials, 6 by each observer, 8 were successful and 10 were failures. All the cements were incorrectly identified in at least one instance, notwithstanding the fact that each observer was allowed to study the slide and his notes as long as he desired. In such an examination as this the observer is unconsciously influenced by a number of factors which should not be taken into consideration; for example, color, density, and purity of the slides, and it is believed that the number of failures would have been even greater if new slides had been prepared for the final test. Nevertheless, certain slight differences in the appearance of the different cements were observed. Thus, Nos. 1149 and 1150 were ground from the same material and could not be identified one from the other, although readily distinguished from all the others by the more jagged particles and lack of uniformity in size. Of the remaining cements, Nos. 946 and 3296 possibly showed slightly distinguishing characteristics, but in general it may be stated that the particles of the different mill products do not show well-marked peculiarities.

IX. APPLICATIONS OF THE AIR ANALYZER

1. ROUTINE MECHANICAL ANALYSES OF DIFFERENT BRANDS OF CEMENT

When the air analyzer had been developed to a satisfactory working condition, a series of routine analyses of different cements was undertaken. Between 40 and 50 different brands have been examined to date, and others are being added to the list as opportunity offers in the course of the regular work.

2. COMPARISON OF THE PRODUCTS FROM VARIOUS TYPES OF FINISHING MILLS

One of the practical uses of the analyzer is its adaptation to the study of the products of different types of grinding machinery. Comparative examinations of this sort can be made without calibration of the analyzer, and from examination of a large number of cements a fairly correct notion may be obtained of the characteristics of different mills. For the most reliable comparisons, however, the tests should be made on cements ground from the same clinker, and we have utilized every opportunity to obtain such comparisons. Similarly, the degree of pulverization of different clinkers in a given mill can be determined, and the effects of hardness and other variables can be studied with the aid of the analyzer more satisfactorily than with the aid of sieves alone.

3. STANDARDIZATION OF REGROUND AND AIR-SEPARATED CEMENTS WHICH ARE TO BE USED IN THE FURTHER INVESTIGATION OF THE VALUE OF FINE GRINDING

One of the most important functions of the air analyzer, at least so far as investigative work is concerned, is that of determining the real fineness of cements in a region which no mechanical sieve can reach. It is believed that this apparatus, or some other means of determining extreme fineness, is a prime necessity in an investigation of the value of fine grinding, and cements are now being prepared in the laboratory by regrinding and by continuous air separation, in tests of which mechanical sieves are of little or no value.

4. ADAPTATION OF THE ANALYZER TO OTHER MATERIALS AND ITS LIMITATIONS IN THIS RESPECT

Experience has shown that the analyzer is equally well adapted to separations of other materials than cement, and in many cases may give more consistent results on other materials. For example, excellent separations have been made of ground quartz, emery, alumina, and other hard-grained materials. A new field of usefulness has recently been found in the testing of molding sands, in

which the ordinary clay and silt determinations are especially important but ordinarily made by crude washing and settling methods. In fact, an investigation of molding sands has just been undertaken by the Bureau in which the analyzer will be used. On the other hand, the present form of analyzer has failed in attempts to separate hydrated lime and certain paint pigments, in which the coarse material appears to consist of compact agglomerates of fine particles, or of soft grains. Thus, attempts to analyze a sample of hydrated lime led to the interesting result that the amount of the 0.001-inch grade was apparently greater than that which passed the No. 200 sieve. Results of the same character were obtained in the separation of red lead, and to a less extent in separations of litharge. These peculiarities lead one to consider more carefully just what is meant by the fineness of such materials. In the present analyzer the abrasion or attrition of particles under the air stream is considerable, sufficient in the case of hydrated lime and red lead to easily reduce a large portion of the coarse material to fine particles, whereas the abrasion which takes place on the No. 200 sieve is comparatively small. The action of the Thompson classifier is also very gentle, and certain pigment separations made with it [10] are apparently open to the same criticism as the sieve tests of such materials, in that the agglomerates are not sufficiently broken up. The question arising in cases of this sort is simply, What are to be considered the ultimate particles in a fineness test; or, in other words, how vigorous an action may be permitted in making the proposed separations? So far as our present analyzer is concerned, the reliability of the separations can readily be determined by continuing the maximum separation to such a point that the rate of loss is appreciably constant. If this rate is high as compared with that for cement, it may be assumed that the treatment is too vigorous for accurate analyses, but if of the same order, then the analyses may be considered satisfactory.

[10] See report of Subcommittee J of Committee D-1 on the Testing of White Paints, Proc. A. S. T. M., 13, pp. 406-447; 1913.

X. UNCOMPLETED PHASES OF THE INVESTIGATION

The rather extensive study of No. 200 sieves, the results of which were published in Technologic Papers Nos. 29 and 42 of the Bureau of Standards,[11] may be considered the first step in a general fineness investigation of cements undertaken by the Bureau about three years ago. The development of the air analyzer to a satisfactory working condition marks the practical completion of the second stage of the investigation. Many things remain to be done with the analyzer, however, not the least important of which is to get it into the hands of other investigators who will eventually determine whether the apparatus can be adapted to routine cement testing or whether it will serve only for special and investigative work; but before new analyzers of this type are constructed, it is desirable that the present form be simplified and made as compact as possible. It is anticipated that these improvements can be made, and work in this connection is under way.

As already intimated, a more critical study of the theory of the analyzer, of possible factors which influence the separations, and of improved methods of calibration will be made as opportunity offers. In addition to these lines of work, three others have suggested themselves as worthy of investigation. The most important of these is the construction of an apparatus capable of still further subdividing the 0.001-inch grade or "flour." As seen by Fig. 12, the flour consists of particles varying from a certain maximum down to vanishing size, and constitutes normally some 30 per cent of the total cement. The actual course of the mechanical analysis curve below this point is unknown, and for some purposes it is important to know whether this portion has a double curvature. A single division somewhere near the middle of this fraction might furnish the desired information. It has been assumed, however, that the upper limit of the 0.001-inch grade is low enough to be well within the hydraulically active material, and for the contemplated investigation of finely ground cements the present line of division will probably answer all purposes. The further sub-

[11] Technologic Paper No. 29, Variations in Results of Sieving with Standard Cement Sieves. Technologic Paper No. 42, The Standardization of No. 200 Cement Sieves.

division of this grade is interesting, particularly in relation to other materials than cement. For example, the Bureau has recently been requested to cooperate with other Government departments in developing a standard "dust" composed of organic material. Such materials will probably present the same difficulties in separation as hydrated lime and certain paint pigments, for which it has been shown that the present form of analyzer is not adapted. It is believed, however, that the analyzer can be modified in such manner as to make these fine separations, and, incidentally, the accomplishment of this result would insure a very much more complete analysis of cement than is now possible.

Another matter which promises to facilitate the standardization of the analyzer and improve the uniformity of results to be obtained from different analyzers is the possible use of some inert material of proper specific gravity for calibrating the separations of the different nozzles. The nominal sizes of separation now have to be determined from observations on several supposedly normal cements, which is not only a laborious process but likely to be in error from unsuspected peculiarities. If some inert, finely ground material of definite physical properties approaching cement in specific gravity and granular condition could be discovered, it could undoubtedly be used to advantage for calibration purposes. The fact that such a material would not give precisely the same results as cement particles would probably be more than offset by the uniformity to be obtained.

The remaining item of interest in connection with the analyzer is the possibility of checking up the three-dimensional measurements by collecting and weighing a known number of particles representing the different sizes of separation and computing the average diameter from a knowledge of the specific gravity. The chief incentive for this undertaking is to make possible the comparison of actual and theoretical separations, which is important in its bearing on the proper method of expressing the sizes of separation. The three-dimensional measurements are not made with great accuracy and the deduction of the so-called true diameters by two entirely independent methods would perhaps shed further light on the apparent increase in reduction factors for the finer grades, as shown in Table 5. The particles of the

0.003-inch grade would, of course, be easier to deal with than the finer particles, and a brief computation will indicate the magnitude of the problem. The average true diameter of the 0.003-inch separation is shown to be approximately 0.002 inch or 0.005 cm. The weight of an average particle is the product of volume and specific gravity, or approximately

$$W = \frac{\pi}{6}(0.005)^3 \times 3.2 = 0.0000002 \text{ g}$$

Assuming the practical limit of weighing to be 0.000001 g., it would require 500 of these particles for an accuracy in weighing of 1 per cent. This would therefore be a comparatively easy experiment to carry out, although this degree of accuracy might not be attained. In the case of the 0.001-inch separation, the weight of an average particle would be of the order of one-thirtieth as great as that computed above, and therefore some 15 000 particles would be required to yield an accuracy of 1 per cent in weighing. It remains to be seen whether the counting and weighing of particles of these dimensions can be done with sufficient accuracy to make the attempt to check the microscopic determinations worth while.

XI. SUMMARY

Summarizing briefly this preliminary report on the air analyzer, we may call attention to the following points of chief importance:

1. The design of a satisfactory elutriator is based on certain fundamental requirements, which have been enumerated. If these requirements are embodied in the construction of a given elutriator, its shape, dimensions, and working conditions are of secondary importance, and can be readily adapted to give the desired separations.

2. A review of earlier types of elutriators used or proposed for cement testing shows that some are faulty in design or unnecessarily complicated, while others are probably capable of making good separations. Only one serious attempt appears to have been made to identify the separations in terms independent of the particular apparatus employed, and this not in a manner to enable comparisons to be made with results obtained by others.

3. After a series of preliminary experiments an air analyzer has been developed at the Bureau of Standards which seems to meet the fundamental requirements and appears to give reliable separations of cement and certain other materials. The distinguishing features of the apparatus are: The introduction of an unretarded air stream into a conical-shaped bulb in such manner that the sample under examination is completely and continuously exposed to the action of the air; a separating chamber of considerable height which permits no lodgment of either fine or coarse particles; a tapping device to minimize the adherence of fine dust to any part of the apparatus; and a collector which catches and holds all material passing through the separating chamber.

4. Believing that the main objection to elutriation methods has been the lack of standardization of apparatus heretofore used, we have endeavored to define the separations obtained by the air analyzer entirely in terms of the limiting sizes of particles in the different fractions. These limiting sizes, designated as the "sizes of separation," may be interpreted in different ways, depending upon the methods of measurement. Several methods of measurement have been studied, and a system has been provisionally adopted, which appears to be the simplest and most direct, although not giving directly the "true diameters" of the particles under examination. The relations between the "apparent" and "true" sizes of particles have been expressed by means of reduction factors, which enable one to convert from one system to another.

5. A preliminary study has been made of the effects of abrasion, specific gravity, atmospheric conditions, and other factors on the separations, but much more work remains to be done before the limitations of the analyzer can be established with certainty. It seems probable that under normal operating conditions the nominal sizes of separation of the analyzer determined by calibrations with normal cements will be within about 5 per cent of the actual sizes. This gives rise to a possible error of about 1.5 per cent in estimating the quantity of any desired fraction from the mechanical analysis curve. As the error in determining the percentage of any given fraction by actual separation in the analyzer is probably not greater than 0.5 per cent, we may assume that the routine

analyses, without special calibrations, will enable us to determine the quantity of particles below a given size in any normal cement within 2 per cent. If greater accuracy is desired in special comparisons or in other important cases, calibrations can be made on the material under examination without excessive labor.

6. Further lines of investigation have been suggested, particularly in modifying the apparatus to yield still finer subdivisions. In making this change it is proposed to adapt the apparatus, if possible, to separations of organic and other powders which are not capable of withstanding the abrasive action produced by the air blast in the present type of bulb and nozzles.

7. The analyzer has been developed with the particular purpose in view of determining the granulometric composition of very finely ground and air separated cements to be used in a further investigation of the value of fine grinding, which is now under way. It is also adapted in its present form to comparisons of the products of different finishing mills and to the separation and grading of abrasives and other hard-grained materials. In view of the considerable variety of finely divided materials already tested with the analyzer, the apparatus promises to have a much broader field of usefulness than that for which it was originally designed.

In conclusion, it is desired to acknowledge the valuable assistance rendered by Allen R. Green in making the three-dimensional microscopic measurements on a very large number of small particles.

WASHINGTON, April 26, 1915.

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EMERGENT STEM CORRECTION FOR THERMOMETERS IN CREOSOTE OIL DISTILLATION FLASKS

BY

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Bureau of Standards

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EMERGENT STEM CORRECTION FOR THERMOMETERS IN CREOSOTE OIL DISTILLATION FLASKS

By R. M. Wilhelm

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I. INTRODUCTION

In many industrial operations where mercurial thermometers are used, the form of the apparatus may prevent the placing of the thermometer so that its entire mercury column is immersed at the temperature of the bulb. Under such conditions the temperature of the stem in general differs from that of the bulb. Thermometers are commonly scaled to read correctly only when the entire mercury column is at the temperature of the bulb, and if used otherwise they will not indicate the true temperature of the bulb unless corrections are applied to their readings. A particular example is that of the use of thermometers in distillation flasks, where the

correction may amount to 15° or 20°[1] under actual distillation conditions.

The magnitude of this correction depends for the greater part on the length and the temperature of the emergent stem (referring only to the part containing the mercury thread). One of the chief sources of error in the use of mercurial thermometers arises from uncertainties as to the temperature of this emergent stem, as it may have as its average almost any temperature between that of the bulb and that of the air in the room, depending upon the conditions under which the thermometer is used.

The emergent stem correction may be computed, provided certain conditions are known, such as average stem temperature, depth of immersion, and the kind of glass of which the thermometers are made. Thermometers tested under conditions of total immersion at the Bureau of Standards are furnished with emergent stem correction sheets which show by example how this correction may be determined, if the instrument is read partially immersed, by using a simple formula. But aside from the general dislike of the use of formulas in industrial operations, in some cases the factors involved (the emergent stem temperature in particular) are difficult to obtain accurately.

Thermometers are sometimes scaled for use or tested with the bulb and only a part of the stem immersed. Such thermometers read correctly, however, only when the temperature conditions under which the thermometers were graduated or tested correspond to those of use, and this is seldom the case. It is obvious that when a thermometer scaled for a given immersion is used at some different immersion its readings will generally be in error.

For some processes it is not of great importance that the thermometer readings should represent the actual temperature of the bulb so long as such processes are confined to a single laboratory and to uniform conditions; but whenever it becomes necessary to specify the conditions under which the processes are carried out, so that they can be repeated elsewhere, a knowledge of the true temperatures becomes necessary.

The purpose of this investigation was primarily to ascertain the magnitude of the emergent stem correction error which may occur

[1] All temperatures in this paper are expressed in degrees centigrade.

in the use of thermometers in the distillation of creosote, a question which has arisen at various times in connection with the testing of thermometers for use in distillation flasks.

Some work has already been done on the subject of emergent stem corrections of thermometers in distillation flasks. In a circular by Dean and Bateman,[2] of the United States Forest Service, on the distillation of coal-tar creosote, there is published a table of emergent stem corrections. Wiebe[3] has also given emergent stem correction tables for thermometers used with glass and with metal distillation apparatus. These tables are considered more fully later.

II. APPARATUS AND METHOD

1. FLASKS AND THERMOMETERS USED

Four types of distillation flasks, as shown in Fig. 1, were used—the retort, recommended by the American Railway Engineering and Maintenance of Way Association; the Hempel flask, as used by the Forest Service; the Lunge side-neck flask, recommended by the Committee on Preservative Treatment of Poles and Cross Arms of the National Electric Light Association; and the ordinary 200-cc side-neck flask, with dimensions as follows: Diameter of bulb 8 cm, diameter of neck 2 cm, height of neck 15 cm, distance from bottom of outlet tube to top 8 cm. All the tests were made according to the specifications[4] applying to the particular form of apparatus used, except where special experiments were made to determine the effect of variations from the specified procedure. A graduated stem continuous scale type of mercurial thermometer, 40 cm long, graduated into 1° intervals from 0° to 400° C, was used. The length of a 1° interval was 0.8 mm; the distance from middle of bulb to 0° mark was 2.5 cm. The thermometer was "filled under pressure" to prevent distillation of the mercury, and was well annealed to prevent a rise of the readings with continued heating.

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[2] Forest Service Circular 112.

[3] Petroleum Jahrgang, VII, 1912.

[4] American Ry. Eng. and Maintenance of Way Assn., 1905, pp. 4–14. National Electric Light Assn. Report on Preservative Treatment of Poles and Cross Arms, 1911, p. 21. Forest Service Circular 98, pp. 8–10. Forest Service Circular 112, p. 37.

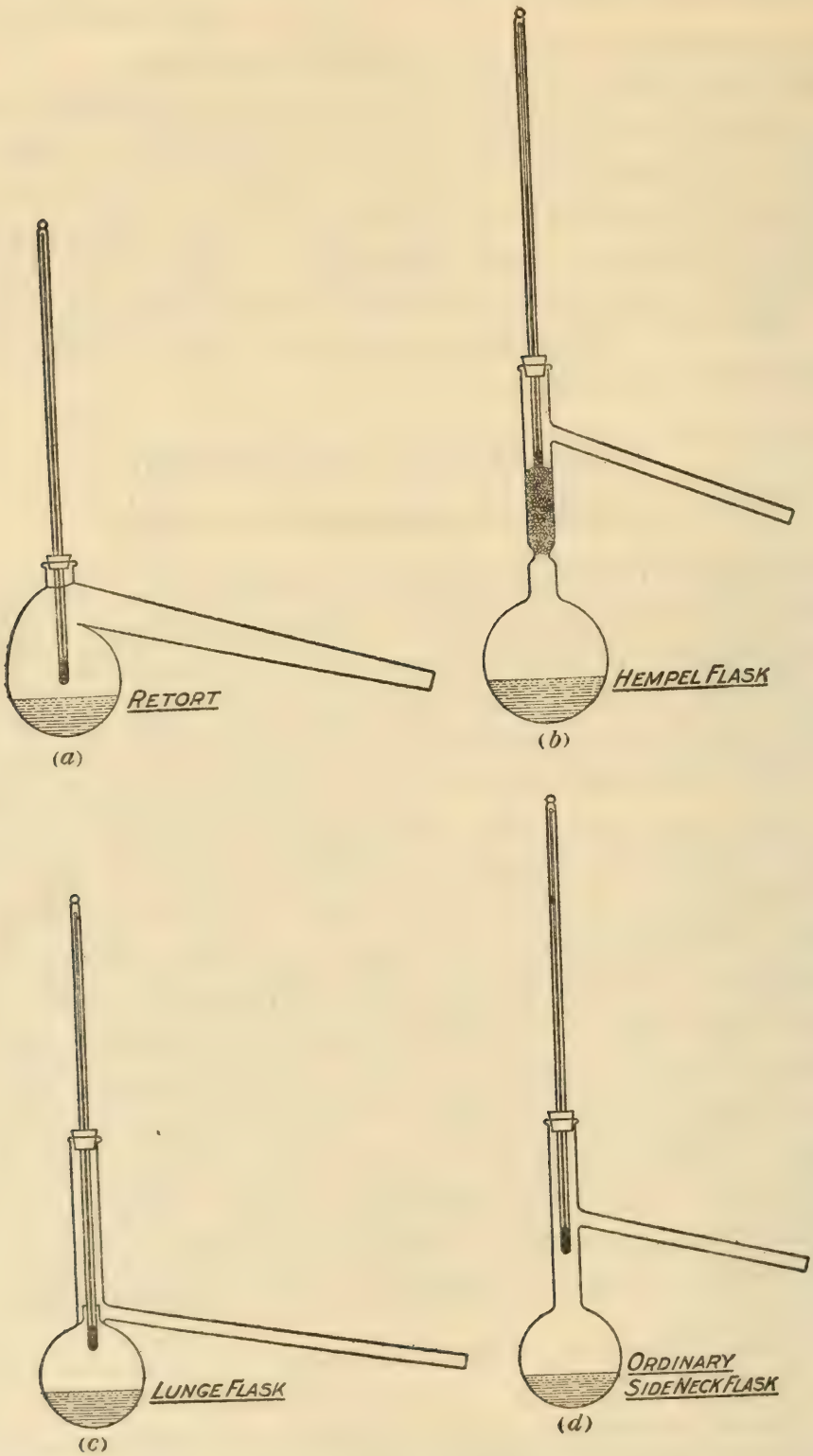

FIG. 1.—*Types of distillation flasks used and positions of thermometers*

2. METHOD USED TO DETERMINE EMERGENT STEM CORRECTION

For measuring the temperature of the stem, use was made of a number of special "thread" thermometers made up and calibrated for this purpose, and auxiliary thermometers for the part of the stem not covered by the thread thermometers. With these thermometers the mean temperature of the emergent mercury column over its entire length could be very closely ascertained. The use of these "thread" thermometers is discussed in detail in a Bureau publication.[5]

Most of the apparatus and the creosote oil were furnished to the Bureau by S. R. Church, of the Barrett Manufacturing Co.

III. RESULTS

1. EMERGENT STEM CORRECTION TABLES

Average emergent stem corrections, applicable for the particular type of thermometer as used in the different distillation flasks, were determined for readings taken on the thermometer at every 20° from 200° up to 350°. The emergent stem corrections found are given in Table 1.

TABLE 1

Stem Corrections for the Thermometer [a] in the Four Types of Flasks

Reading	Retort	Hempel flask	Lunge flask	Ordinary flask
Degrees	Degrees	Degrees	Degrees	Degrees
200	+ 4.8	+ 4.7	+ 5.2	+ 4.7
220	+ 5.8	+ 5.0	+ 6.1	+ 5.0
240	+ 7.1	+ 6.1	+ 7.2	+ 5.4
260	+ 8.5	+ 7.5	+ 8.4	+ 6.6
280	+10.0	+ 8.5	+ 9.7	+ 8.5
300	+11.8	+10.5	+11.5	+10.5
320	+13.7	+12.4	+13.5	+12.5
340	+15.7	+14.4	+15.8	+14.5
350	+16.8	+15.5	+17.1	+15.5

[a] These corrections apply only for a thermometer similar to that used in these tests.

The corrections are given to tenths of a degree, but an inspection of the curves plotted for the different runs shows that for the same reading the emergent stem correction may differ by over a degree from one curve to another. For this reason the corrections may not be reliable to better than a degree.

[5] E. Buckingham, Bulletin Bureau of Standards, 8, p. 239.

2. EMERGENT STEM CORRECTION CURVES

The separate observations from which Table 1 was obtained have been plotted for the different types of flasks in Figs. 2, 3, 4,

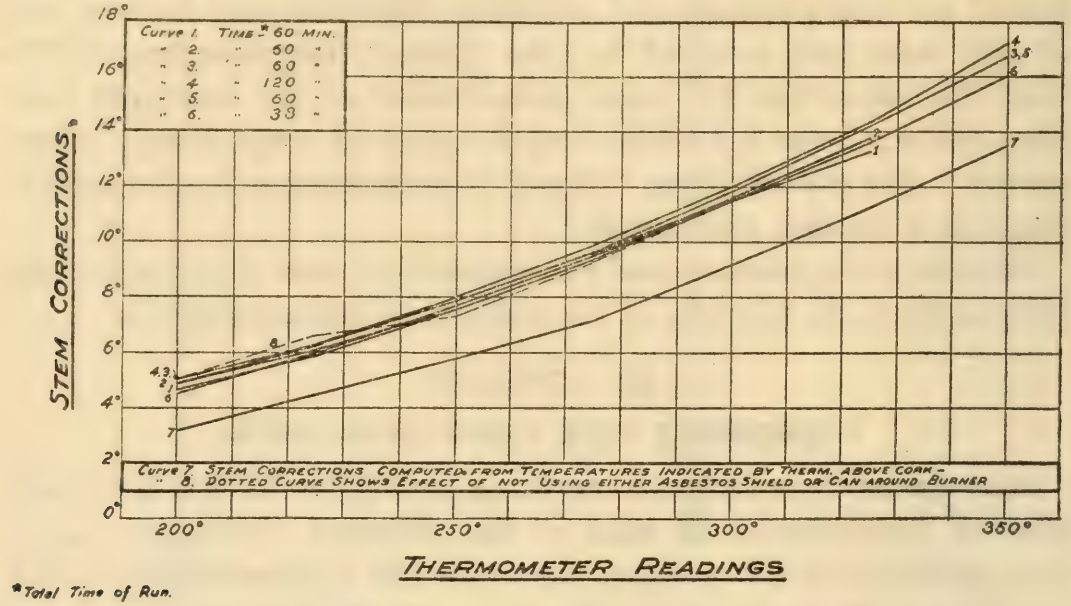
Curve 1. Time* 60 Min.
" 2. " 60 "
" 3. " 60 "
" 4. " 120 "
" 5. " 60 "
" 6. " 33 "
Curve 7. Stem Corrections Computed from Temperatures Indicated by Therm. Above Cork.
" 8. Dotted Curve Shows Effect of not Using either Asbestos Shield or Can around Burner
Stem Corrections°
Thermometer Readings
200°
250°
300°
350°
*Total Time of Run.

FIG. 2.—*Stem corrections using retort*

and 5. From the curves it would seem that, of the four types of flasks, the retort gives the most nearly uniform results as regards

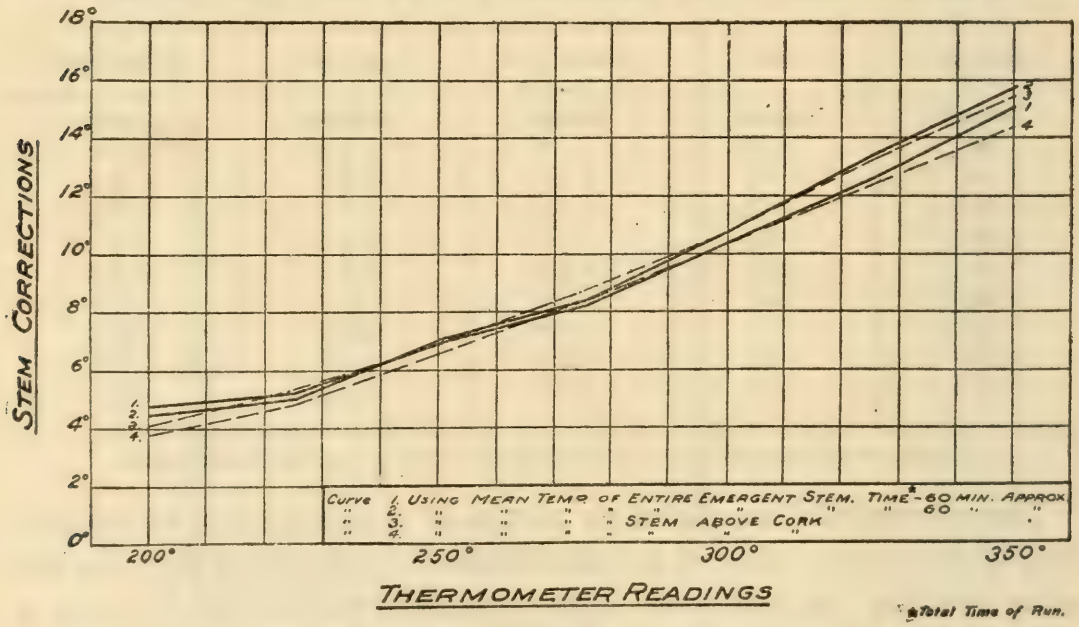
Curve 1. Using Mean Temp. of Entire Emergent Stem. Time*-60 Min. Approx.
" 2. " " " " " " " 60 " "
" 3. " " " Stem above Cork " " "
" 4. " " " " " " "
Stem Corrections
Thermometer Readings
200°
250°
300°
350°
*Total Time of Run.

FIG. 3.—*Stem corrections using Hempel-flask*

emergent stem corrections. This may be due to the fact that practically the entire retort is covered by the asbestos shield.

The agreement between the emergent stem corrections observed in different runs is next best in the Hempel flask and worst in the

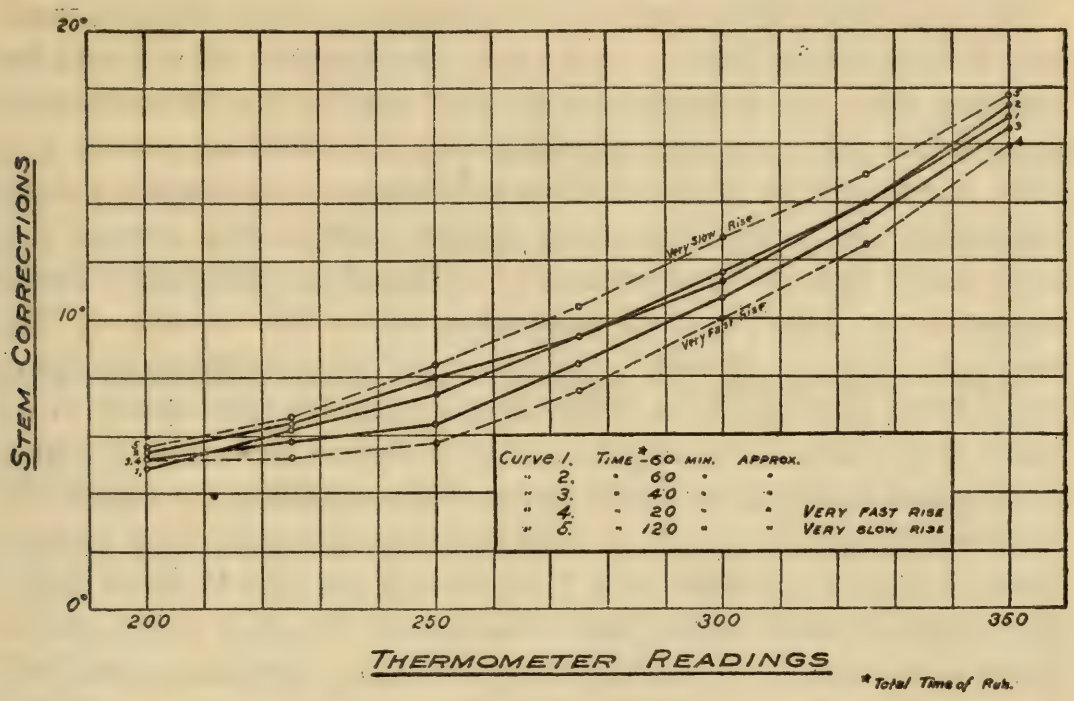

FIG. 4.—*Stem corrections using Lunge flask with trap*

ordinary side-neck flask, although the irregularity of several of the curves in this case was due to moisture in the oil and to increas-

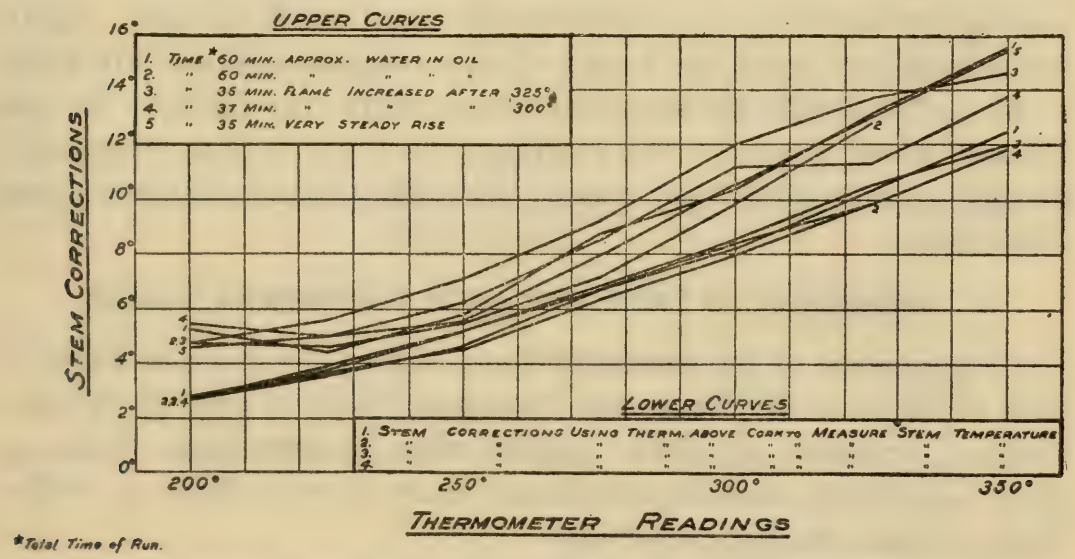

FIG. 5.—*Stem corrections using ordinary side-neck distillation flask*

ing the size of the flame. The constancy of the emergent stem corrections in the retort should not be taken as a recommendation

of this form of apparatus, since there are apparently some very decided disadvantages in its use.[6]

The true mean temperature of the emergent stem of thermometers in distillation flasks is not easily obtainable. If it could be assumed that the temperature of that part of the thermometer stem below the cork were uniform and the same as that of the bulb, the emergent stem could be considered as that part within and above the cork. The mean temperature of this part of the stem could then be approximately obtained by hanging a small thermometer with its bulb somewhat below the middle of the emergent mercury thread. The emergent stem corrections computed from readings of a thermometer with its bulb about two-thirds way down the emergent mercury thread have been plotted for three of the flasks and the curves thus obtained are shown on the same figures (2, 3, and 5) with the true emergent stem correction curves. It may be seen that, except for the Hempel flask, the emergent stem corrections obtained by the two methods are not in agreement. As would be expected, the corrections obtained by neglecting the part of the stem below the cork are, with the exception mentioned, too low, since they do not take account of the temperature conditions below the cork. Thus, in the ordinary flask, the emergent stem corrections, using the stem temperature as indicated by a thermometer hung with its bulb about two-thirds way down the length of the emergent column, are from 1° to 2.5° less than the actual emergent stem corrections. In the Hempel flask, however, the emergent stem corrections computed in this manner agree very closely with the actual emergent stem corrections.

3. COMPARISON OF EMERGENT STEM CORRECTION TABLES

A comparison of the emergent stem corrections given in Table 1 with those given by Dean and Bateman, Table 2, and by Wiebe, Table 3 (column 2), show considerable disagreement. Table 3 gives corrections considerably larger than those in Table 1, while Table 2 gives smaller corrections.

Dean and Bateman probably used a thermometer graduated from 200° up, with an enlargement in the stem below the 200°

[6] Alleman, Forest Service Circular 98, p. 8. Dean and Bateman, Forest Service Circular 112, p. 35.

mark. Wiebe does not state the type of thermometer used in his investigation, but it probably was one of the inclosed scale type (einschluss). The Engler flask used by Wiebe is smaller than the flasks used in this investigation.

The corrections in Table 3, column 3, were obtained by Wiebe for a thermometer used in a metal distillation apparatus. The question of emergent stem corrections in metal distillation apparatus was not taken up in this investigation, as this type of flask is little used in this country.

TABLE 2

Dean and Bateman's Corrections for the Emergent Thermometer Stem in 500-cc Side Neck Flask

Thermometer reading	Stem temperature	Degrees emergent	Correction	Corrected reading
Degrees	Degrees	Degrees	Degrees	Degrees
210	42.0	10	+0.3	210.3
220	43.5	20	.6	220.6
230	45.0	30	.9	230.9
240	47.0	40	1.2	241.2
250	48.5	50	1.6	251.6
260	50.0	60	2.0	262.0
270	52.0	70	2.4	272.4
280	53.5	80	2.9	282.9
290	55.0	90	3.4	293.4
300	57.0	100	3.9	303.9
310	58.5	110	4.4	314.4
320	60.0	120	5.0	325.0

TABLE 3

Wiebe's Corrections for the Emergent Thermometer Stem in Engler Flask and Metal Apparatus

Temperature	Stem correction—		Temperature	Stem correction—	
	In glass apparatus	In metal apparatus		In glass apparatus	In metal apparatus
Degrees	Degrees	Degrees	Degrees	Degrees	Degrees
60	+0.8	+0.2	200	7.2	4.3
80	1.6	.5	220	8.7	5.4
100	2.3	.9	240	10.3	6.6
120	3.1	1.4	260	12.2	8.0
140	3.9	1.9	280	14.1	9.3
160	4.9	2.6	300	16.3	10.6
180	5.9	3.4	320	18.8	11.9

Wiebe states that the results of distillation tests made with the metal and the glass apparatus are not comparable, owing to the fact that the vapor in the two types of apparatus is at different temperatures for the same temperature of the liquid. An example is given in which the temperature of the liquid was 178° in each type of apparatus, while the temperature of the vapor was 150° in the metal apparatus, but only 136° in the glass apparatus. Wiebe concludes that even though the readings in the two apparatus are corrected, the fractions at the lower temperature will be different and hence a standard method of distillation is necessary.

Tables of stem corrections have very little value unless it is certain that the thermometers used and the conditions under which the tests are made are similar to those for which the tables were computed.

IV. REASONS FOR VARIATIONS IN STEM CORRECTIONS

Using any one type of flask, differences in the emergent stem correction for a given reading of the thermometer may be caused by the following: (1) Unsuitable thermometers; (2) variations in rate of rise of temperature.

1. UNSUITABLE THERMOMETERS

Thermometers having an enlargement in the capillary between the ice point and the scale so that the graduations shall begin at a higher temperature, say 200°, should not be used in distillation flasks, unless the conditions are such that the temperature of the enlargement is the same as that of the bulb.

Although with such a thermometer the emergent stem correction is smaller, its variations may be larger, due to variations in the temperature of the enlargement under different conditions of use.

2. VARIATIONS IN RATE OF RISE OF TEMPERATURE

The rate of rise can be controlled fairly well, and as is seen from the curves (particularly Fig. 4), the faster the rate of rise, the smaller the emergent stem correction. This is due to the fact that for a faster rate of rise the flask and the air above it become hotter, due to the larger flame used. Care should therefore be taken that the rate of rise is controlled according to specifications.

V. EFFECT OF RADIATION AND OF CONDENSED VAPOR ON TEMPERATURE MEASUREMENTS

While discussing variations due to emergent stem corrections it is not out of place to call attention to other causes of variation in the indications of the thermometer, such as (*a*) heating of the bulb by radiation from the hotter oil and (*b*) cooling of the bulb due to radiation to colder objects and to the condensing oil which runs down over the bulb.

The magnitude of the error due to radiation from the oil and hot flask is difficult to ascertain, and is probably negligible except where the bulb and stem are close to the oil. It seems desirable for this reason to have the thermometer bulb at some distance above the level of the oil.

Table 4 shows the magnitude of the cooling effects for one type of flask. Two thermometers were read simultaneously, one being shielded, the other not. A perforated conical aluminum shield, having a length about equal to that of the bulb and fitting tightly around the stem just above the bulb, was used. The difference between the indications of the shielded and the unshielded thermometers amounted to as much as 3°. This experiment shows the cooling effect on the bulb only; the effect on the stem is entirely negligible. Varying amounts of condensing oil vapor will cause variations in the readings for the same temperature of the vapor. It is probably inconvenient in industrial work to eliminate this source of error in the present type of distillation flask.

TABLE 4

Effect of Radiation and Condensed Vapors on Thermometer Reading

Readings	Difference between thermometer readings, neither thermometer shielded	Difference between readings, one thermometer shielded	Effect of shielding
Degrees	Degrees	Degrees	Degrees
200	+1.0	0.0	+1.0
225	.0	−3.0	+3.0
250	.0	−2.5	+2.5
275	+ .2	−3.0	+3.2
300	+ .5	−2.5	+3.0
325	− .5	−3.0	+2.5
350	−1.2	−3.0	+1.8

VI. EFFECT OF ERROR IN TEMPERATURE MEASUREMENT ON FRACTIONS DISTILLED

It is evident, since the amount of distillate increases with increasing temperature, that, using the same sample of oil, if at one time a fraction is taken off at a certain temperature and at another time this fraction is taken off at a different temperature, the results in the two cases will not agree.

The specifications by which distillation tests are governed state that the fractions shall be taken off at certain specified temperatures, which are to be read off on a thermometer the type of which is also specified. From the previous discussion of the subject of emergent stem corrections it is obvious that unless this correction is taken account of the results obtained by assuming that the reading on the thermometer represents the specified temperature will depend not only upon the reading of the thermometer, but also upon the conditions of stem temperature prevailing at the time of test. On the other hand, if the specified temperatures are taken to mean the temperature of the bulb of the thermometer, and fractions are taken off at readings on the thermometer which represent the specified temperature of the bulb, the results obtained will not agree with those obtained by taking off the fractions at uncorrected readings.

It was at first intended to run a series of distillations under these two conditions and to compare the results thus obtained; later it was decided that a very good idea of the magnitude of the disagreement between the two methods could be obtained from the data on percentage distillates published by the National Electric Light Association in their report of June 2, 1911. From the data a curve was drawn representing the percentage distillates for the Lunge flask corresponding to various thermometer readings. Using this curve, two series of percentage distillates were taken off. In the first case the specified temperatures were taken to mean thermometer readings; the fractions were therefore taken off at readings 170°, 205°, 245°, etc. (Table 5); in the second case the specified temperatures were taken to mean bulb temperatures and the fractions were taken off at readings 166°, 200°, 238°, etc. (Table 6), these readings being those which correspond to bulb temperatures of 170°, 205°, 245°, etc.

TABLE 5

Fractions	I	II	III	IV	V	VI	VII
Points specified	to 170°	to 205°	to 245°	to 270°	to 320°	to 360°	above 360°
Per cent distillate	1.4	3.6	54.0	67.6	82.5	92.1	99.5

TABLE 6

Fractions	I	II	III	IV	V	VI	VII
Points specified	to 170°	to 205°	to 245°	to 270°	to 320°	to 360°	above 360°
Readings on thermometer to give specified temperature of bulb	[a] 166°	200°	238°	262°	308°	344°	344°
Per cent distillate	[a] 1.0	3.2	46.8	63.5	79.4	88.0	99.5

[a] Extrapolations.

The differences between the fractions using the two methods are given below.

TABLE 7

Fraction	I	II	III	IV	V	VI	VII
Differences in per cent distillates	0.4	0.4	7.2	4.1	3.1	4.1	0.0

The above figures must be taken as only illustrative of the effect of taking into account or disregarding emergent stem corrections and should not be used as a means for correcting results.

VII. A SUGGESTED METHOD OF TESTING THERMOMETERS USED IN DISTILLATION APPARATUS

The total correction which must be applied to the readings of a thermometer used in a distillation flask to reduce these readings to those corresponding to the temperature of the vapor may be considered as made up of three parts—(*a*) the scale correction, i. e., the correction to the reading of the thermometer which could be obtained by comparing its readings when totally immersed with the corrected readings of a standard thermometer; (*b*) the emergent stem correction, which, as heretofore explained,

is the correction due to the emergent stem; and (*c*) the corrections which should be applied to allow for effect of condensing oil and of radiation. Tables of emergent stem corrections have been previously given, and the application of these corrections to the thermometer readings would suffice to reduce the readings to true temperatures, if it could be assumed that the other corrections mentioned above were negligible. This is seldom the case, however, as the scale correction itself in some cases might exceed 5°. To provide a means whereby the total correction may be determined to an accuracy sufficient for most oil distillations—i. e., about 1° or 2°—the following method is suggested:

The method involves the boiling, in the distillation flask to be used, of certain substances of known "boiling points." For distillations above 200° the substances suggested are naphthalene, B. P. 218°, and anthracene, B. P. 340°. The thermometer to be tested is placed as for a distillation test and read with its bulb immersed in the vapors of these substances. The difference between the temperature of the vapor and the reading will be the total correction to the thermometer at these two points, provided the conditions correspond to those of an actual distillation, and if this correction could be considered as changing linearly a straight line drawn between the two corrections plotted on coordinate paper would represent the total corrections to the thermometer at intermediate points. It has been shown, however, that one of the factors in the total correction, viz, the emergent stem correction, does not change linearly with respect to temperatures. An inspection of the correction curves in Figs. 2, 3, 4, and 5 shows that the curves depart from a straight line by as much as 2°, and hence, if a greater accuracy than this is desired, an allowance for this curvature must be made. Fig. 6 shows the result of a calibration by this method of one of the thermometers used in this investigation. Its scale corrections were already known. Its reading in the vapor of naphthalene was 214°, in anthracene vapor 329°; the total correction at the reading 214° was therefore +4°, and at 329°, +11°. The dotted line in Fig. 6 is a straight line drawn between the two corrections for readings at 214° and 329°. In drawing the solid line allowance has been

made for the fact that the emergent stem corrections do not change linearly. In this method the scale correction and the corrections mentioned on page 16 must be considered as changing linearly between the two readings, unless the scale corrections have been previously determined, in which case allowance may be made if these scale corrections do not change uniformly.

For the convenience of those who may use this method, a table of "deviation" corrections is given, namely, Table 8. These corrections were obtained by plotting a curve corresponding to the

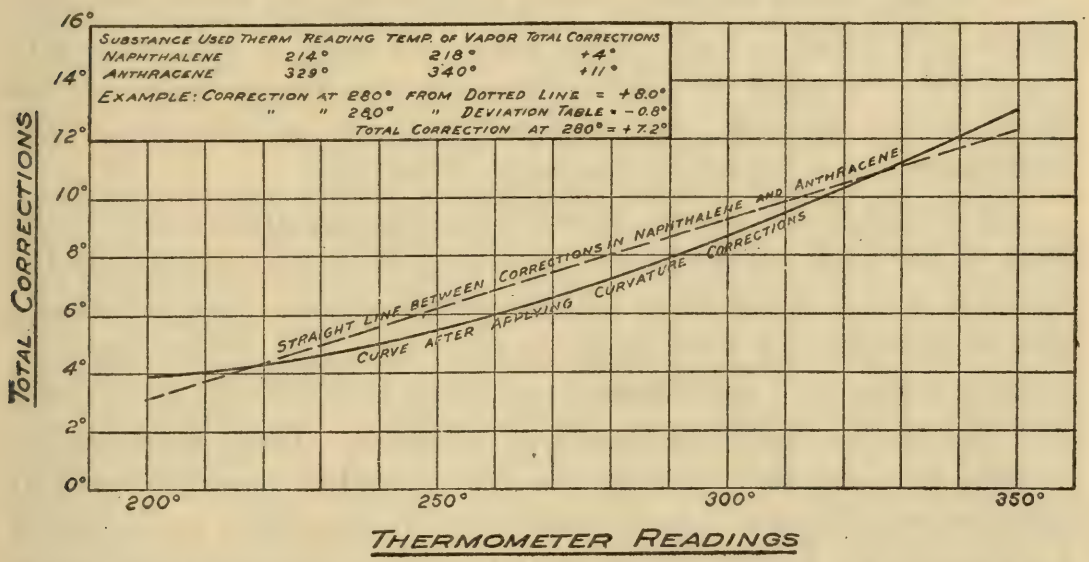

FIG. 6.—*Total correction curve. Thermometer used in ordinary side-neck distillation flask*

average of the emergent stem corrections given in Table 1 for the four types of flasks and finding the amount that the curve thus obtained deviated from a straight line passing through readings corresponding to temperatures of 218° and 340°.

TABLE 8

Deviation Corrections

Readings	200°	220°	240°	260°	280°	300°	320°	340°	350°
Corrections	+0°.7	−0°.1	−0°.6	−0°.8	−0°.8	−0°.6	−0°.2	+0°.4	+0°.7

To find by this method, then, the total corrections to a thermometer in a distillation flask, first find the total corrections to

the thermometer for readings in naphthalene and anthracene, then from these two corrections construct a table or a plot representing a series of corrections changing linearly between 200° and 350°. Finally, to allow for the nonuniformity of the stem correction curve, add algebraically to the corrections found by linear interpolation, as indicated above, the deviation corrections given in Table 8, and the resulting corrections will be the total corrections to the thermometer, within certain limits of error which have already been discussed.

In boiling either naphthalene or anthracene the condensed substance will solidify in the outlet tube and close it, and, except in the retort, the vapor will then rise in the neck of the flask. If the flame is hot enough, the condensation line of the vapor will eventually reach the top of the neck of the flask.

The height of the vapor of napththalene and anthracene in the neck of the flask should be the same as it is in the creosote-oil distillation; but as in the latter case the condensation line is not sharp, special experiments were made to determine just where the condensation line with naphthalene and anthracene should be in order that the above condition should be satisfied. These experiments showed that the thermometer should be read in naphthalene and anthracene when the line of condensation reached a point about 3 cm above the bottom of the outlet tube (in the retort the top is about 3 cm above the bottom of the outlet tube).

The following directions should be observed in determining the total corrections of a distillation thermometer by measurements in the vapors of boiling naphthalene and anthracene:

1. The flask must be shielded and the thermometer placed according to the specifications for distilling creosote oil with the type of flask used.

2. The substance (naphthalene or anthracene) must be melted and boiling commenced slowly, and the thermometer must be read when the condensation line reaches a point 3 cm above the bottom of the outlet tube.

3. Care must be taken that there is an opening in the cork to insure that there shall be no excess of pressure inside the flask.

The method was not applied to the Hempel flask with beads in the neck. There may be some difficulty in this case owing to the

clogging of the beads by the solidified anthracene, necessitating special heating of the neck of the flask.

VIII. THE BOILING POINT OF ANTHRACENE

The boiling point of naphthalene has been accurately determined. The boiling point of anthracene was not known accurately. A series of observations showed that in the glass flasks the temperature of the vapor is 340° at standard atmospheric pressure. Investigation showed that the ordinary purified yellow anthracene could be used in obtaining the boiling point of the substance. A limited number of experiments showed no significant difference between the boiling point of the yellow variety and the most highly purified white material. The temperature was measured with both a mercurial thermometer and a thermocouple. The mean gave 340° as the temperature of the vapor of anthracene boiling at standard atmospheric pressure and it can probably be depended upon to 1°. The temperature of boiling substances is influenced by changes in atmospheric pressure. The temperature of boiling water increases approximately 0°.04 per millimeter increase of pressure, naphthalene 0°.05 per millimeter, and anthracene 0°.07 per millimeter. This last figure is only approximate and was computed from the known relations between boiling points and pressures. It can be seen that in the case of naphthalene and anthracene a range of variation of a degree in the temperature of the vapor is possibly due to variations in the local barometric pressure. However, if a barometer is not at hand, the correction can be assumed to be negligible under normal weather conditions for localities not more than a few hundred feet above sea level.

IX. SUMMARY

Emergent stem correction errors in creosote oil distillation flasks are discussed, and corrections applicable to a particular type of thermometer when used in any one of four different types of distillation flasks were determined. Tables of corrections are given applicable to these four types of flasks.

The emergent stem correction may amount to as much as 17° at 350°.

The emergent stem corrections applicable to the different types of flasks do not differ much from each other for similar thermometers read at the same temperature, the greatest difference being 2°. This is one reason why the published results of distillation tests made with different types of flasks agree fairly well. From the standpoint of temperature measurement and in particular emergent stem correction there is therefore little to choose between the different types of flasks.

The most desirable type of mercurial thermometer to use is probably the continuous-scale graduated-stem type divided into degrees, the length of a degree interval being about 0.8 mm. The thermometer should be "filled under pressure" to prevent distillation of the mercury, should be well annealed to prevent a rise of the readings with continued heating, and, if possible, should have its scale corrections determined by a standardizing laboratory. The undesirability of using a thermometer with an enlargement in the stem between the bulb and the scale has been discussed. Thermometers could be scaled to read correctly when immersed to the point at which they were to be used in distillation flasks by making use of the corrections obtained in this paper. However, owing to the confusion which might arise in the use of such instruments and the difficulty which would be encountered in attempting to graduate or test them, such a procedure is hardly thought justified at the present time.

A method suggested for finding the total correction to thermometers used in distillation flasks by reading the thermometer first in the vapor of boiling naphthalene and then in the vapor of boiling anthracene was investigated and found to be practicable and sufficiently accurate (about 1° or 2°) for distillation practice.

A significant disagreement in the fractions will result if corrections are made in one case for emergent stem and not in another.

As a final conclusion, it might be said that even if the methods suggested here are not adopted the investigation will at least call attention to the great possibility of wide disagreement in the results obtained in different commercial practices where mercurial thermometers are used with utter disregard to the emergent stem correction errors. To repeat what has already been said,

how can the results in different laboratories be expected to check when in one case a correction is made for the emergent stem, in another it is not, and in another perhaps a thermometer scaled for partial immersion may be used under conditions totally different from those for which it was intended? It is to be hoped that this paper will assist in bringing about greater uniformity in the making of distillation tests, especially from the standpoint of temperature measurements.

WASHINGTON, March 29, 1915.

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
S. W. STRATTON, Director

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS, NO. 50

[Issued September 25, 1915]

VISCOSITY OF PORCELAIN BODIES HIGH IN FELDSPAR

A. V. Bleininger and C. S. Kinnison

The present work is a continuation of the experiments reported in Technologic Paper No. 30 in which the elongation of porcelain bars, subjected to a tensile stress of 5 pounds per square inch, was studied in connection with variations in composition and at several temperatures.

The object of the work was to determine the range of compositions showing greatest rigidity, at the highest kiln temperatures, information which should be useful in selecting bodies subject to minimum deformation in firing, and hence causing least loss in manufacture due to deformed ware.

The shape of the specimen was different from the one used in the earlier study and is shown in Fig. 1. This test piece proved to be very satisfactory. The compositions of the porcelains thus studied were intended to include higher feldspar contents and have been compiled in the following table:

TABLE 1

Composition of Bodies

Number	Clay	Feldspar	Flint	Number	Clay	Feldspar	Flint
	Per cent	Per cent	Per cent		Per cent	Per cent	Per cent
1	35	30	35	10	45	30	25
2	35	40	25	11	45	35	20
3	35	50	15	12	45	40	15
4	35	60	5	13	45	50	5
5	35	65	.....	14	45	55	.....
6	40	30	30	15	50	30	20
7	40	40	20	16	50	40	10
8	40	50	10	17	50	45	5
9	40	60	.....	18	50	50	.....

The clay content was made up of North Carolina kaolin, Georgia kaolin, and Tennessee No. 3 ball clay in the ratios of 5 : 1 : 1. The feldspar used was an average grade of potash spar, and was the same used in the previous work. The bodies were prepared by grinding wet in the ball mill and filter pressing. Plaster molds were used in pressing the specimens. After the pieces were dry, fine shrinkage marks were made on them 4 inches apart. All of the specimens were first burned to cone 10. The fire-clay load pieces to be attached to the lower end of the specimens were made at first to weigh 5 pounds, but it was found that this weight was entirely inadequate, since no deformation was obtained at all. Burns were made then with pieces giving 7.5 and finally 14.5 pounds per square inch. This weight was adopted as the standard condition for this series.

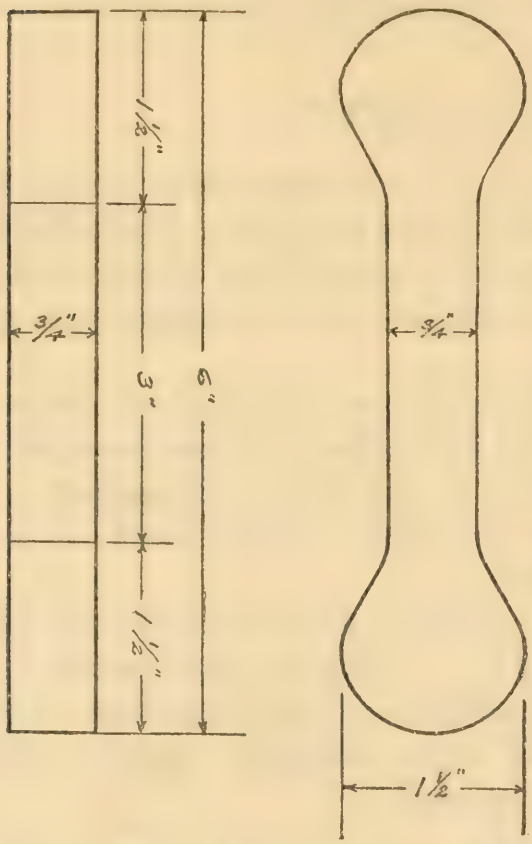

FIG. 1.—*Shape of test piece used in deformation experiments*

This shows clearly that the bodies previously studied, containing from 10 to 25 per cent of feldspar, show far less resistance to deformation under tensile stress than the present series with higher feldspar contents. This would appear to be logical from the viscous nature of the feldspar. Several runs, made below 1275° C, showed contraction; elongation due to softening was first observed at this temperature. It is quite probable that contraction and elongation practically neutralized each other within this temperature region. The pieces were hung from fireclay grids, the weight pieces attached and the kiln brought to the desired temperature at the rate of 30° C per hour. All bodies were vitrified and nonabsorbent. The lengthening of the pieces is expressed in terms of the length after the biscuit burn at cone 10.

RESULTS.

The results obtained are compiled in Table 2, and for bodies Nos. 8 to 18 are shown graphically in Figs. 2, 3, and 4. In the 35 per cent clay series a number of pieces were found to be broken at the higher temperatures, indicating that with low clay content low tensile strengths are obtained. This is to be expected, since

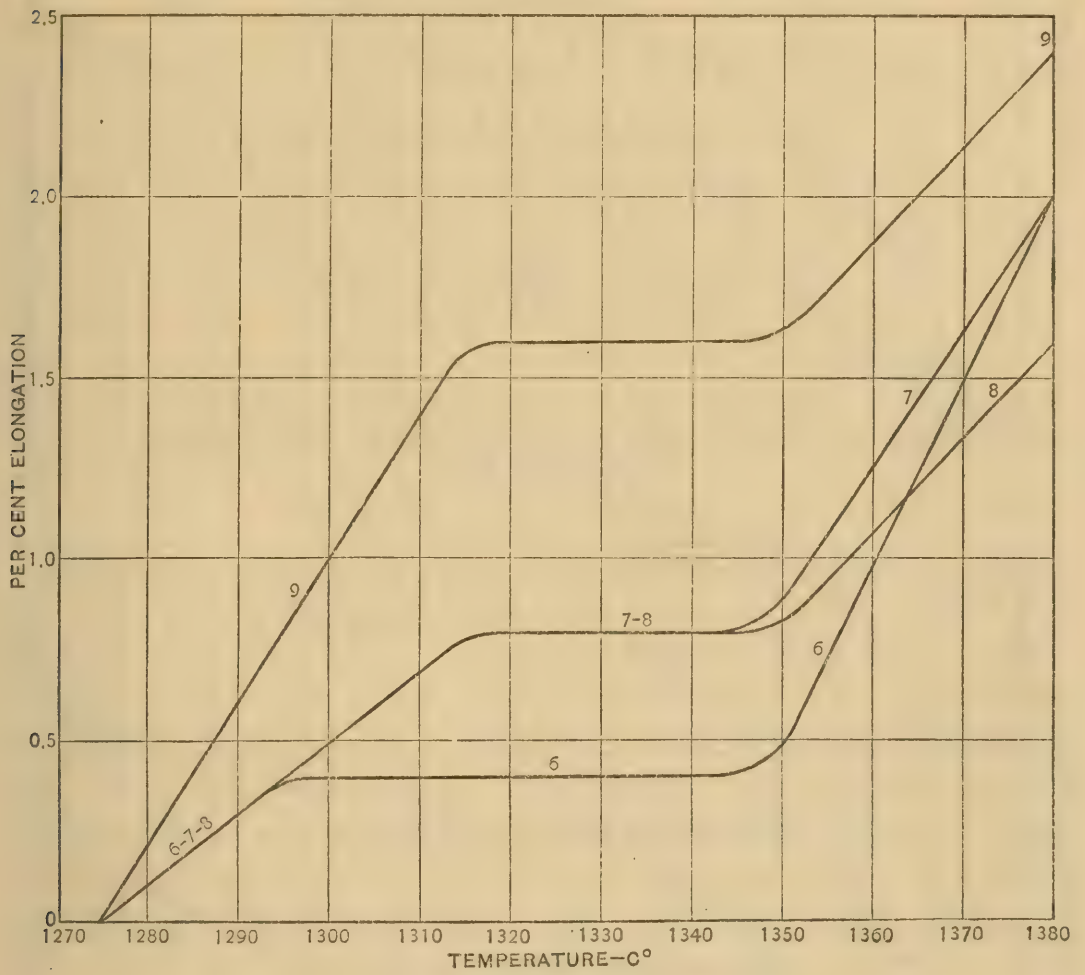

FIG. 2.—*Elongation of 40 per cent clay series*

in the previous series a load of 5 pounds per square inch was sufficient to bring about decided deformation. The results, although incomplete, bring out quite clearly the fact that with low clay content high percentages of feldspar are effective in reducing the rigidity or viscosity of the body. At the temperatures involved such bodies are far more subject to deformation than those having a higher clay content.

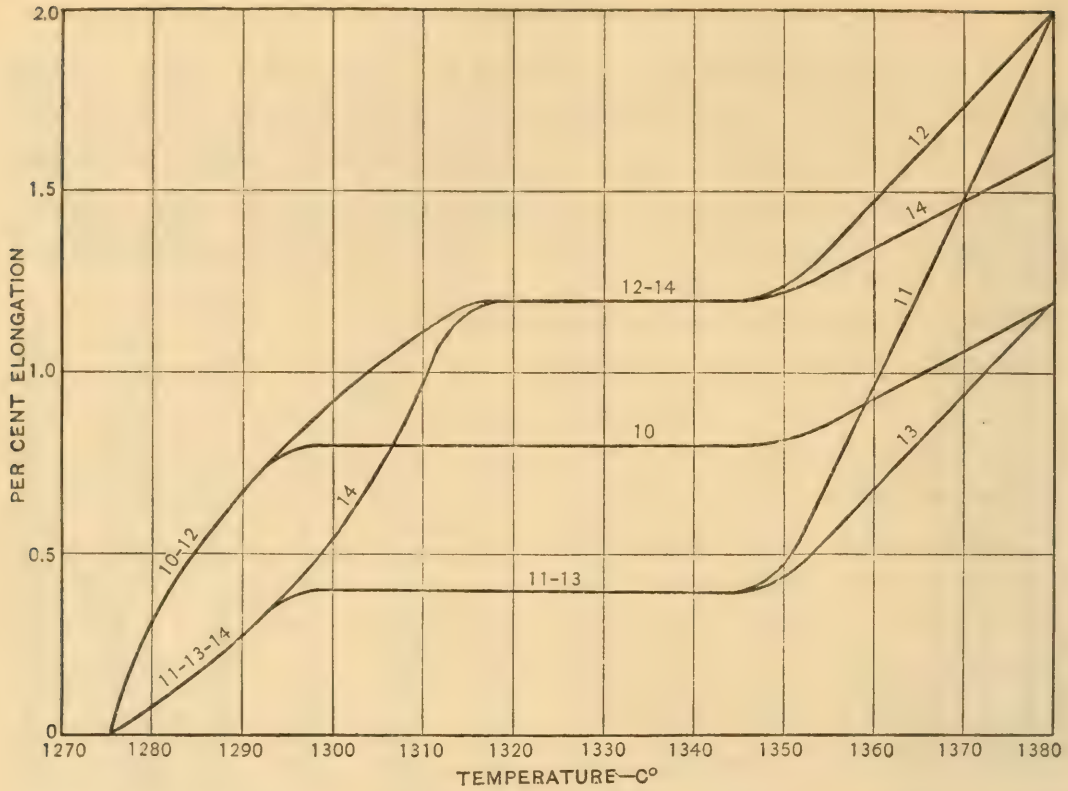

FIG. 3.—*Elongation of 45 per cent clay series*

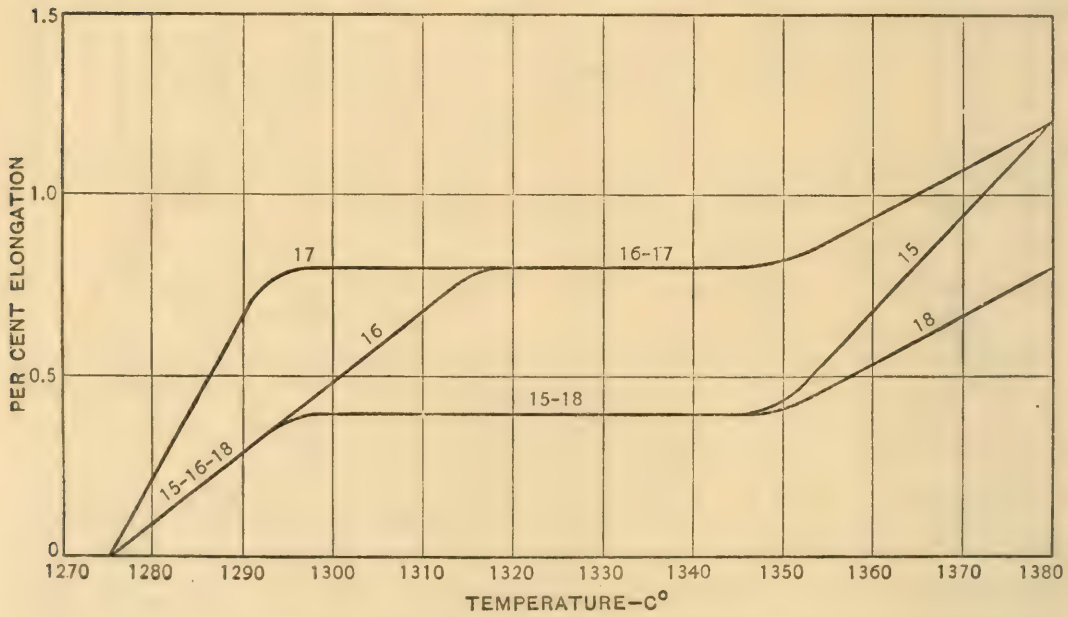

FIG. 4.—*Elongation of 50 per cent clay series*

TABLE 2

Elongation Measurements

Number	Biscuit length	Length, 1275°	Length, 1295°	Length, 1315° 1320°	Length, 1345° 1350°	Length, 1380°	Elong., 2175°	Elong., 1295°	Elong., 1315° 1320°	Elong., 1345° 1350°	Elong., 1380°
							Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
1	2.56	2.56	2.56	2.62	2.66	Broke.	0.0	0.0	2.3	3.9	.....
2	2.56	2.57	2.59	2.62	Broke.	.....	.4	1.2	2.3	.....	.....
3	2.48	2.48	2.49	2.50	2.54	Broke.	.0	.4	.8	2.4	.....
4	2.51	2.51	2.53	Broke.	.....	.....	.0	.8	.....	.....	.....
5	2.51	2.51	2.53	2.55	Broke.	.....	.0	.8	1.6	.....	.....
6	2.50	2.50	2.51	2.51	2.51	2.55	.0	.4	.4	.4	2.0
7	2.49	2.49	2.50	2.51	2.51	2.54	.0	.4	.8	.8	2.0
8	2.48	2.43	2.49	2.50	2.50	2.52	.0	.4	.8	.8	1.6
9	2.50	2.50	2.52	2.54	2.54	2.56	.0	.8	1.6	1.6	2.4
10	2.46	2.46	2.48	2.48	2.48	2.49	.0	.8	.8	.8	1.2
11	2.49	2.49	2.50	2.50	2.50	2.54	.0	.4	.4	.4	2.0
12	2.46	2.46	2.48	2.49	2.49	2.51	.0	.8	1.2	1.2	2.0
13	2.44	2.44	2.45	2.45	2.45	2.47	.0	.4	.4	.4	1.2
14	2.46	2.46	2.47	2.49	2.49	2.50	.0	.4	1.2	1.2	1.6
15	2.45	2.45	2.46	2.46	2.46	2.48	.0	.4	.4	.4	1.2
16	2.44	2.44	2.45	2.46	2.46	2.47	.0	.4	.8	.8	1.2
17	2.43	2.43	2.45	2.45	2.45	2.46	.0	.8	.8	.8	1.2
18	2.44	2.44	2.45	2.45	2.45	2.46	.0	.4	.4	.4	.8

From the observations upon the 40 per cent clay series it appears that the greatest degree of softening is reached with 60 per cent feldspar (no flint). The presence of flint increases the viscosity. Of bodies Nos. 6, 7, and 8 the ones containing 30 and 40 per cent of feldspar seem to reach about the same degree of viscosity at the maximum temperature. The greatest rigidity at the highest temperature seems to be shown with a feldspar content of 50 per cent. At 1345° C, body No. 6, consisting of 30 per cent feldspar and 30 per cent flint, is most rigid. Of considerable interest in this set of curves is the fact that three distinct viscosity stages are recognized. At first, softening is observed which at from 1295 to 1315° C changes to a state of rigidity, since no further elongation is noted. This condition remains constant up to 1345° C, from which point on a decided loss in rigidity is noted and the elongation becomes quite marked. This would seem to indicate further solution of flint and clay by the feldspar, resulting in a viscous magma able to resist deformation. At 1345° the temperature, however, is sufficiently high to bring about softening of the entire mass. According to the viscosity attained between

about 1300° and 1345° three classes of bodies may be recognized, comprised, respectively, of No. 6, Nos. 7 and 8, and No. 9. The first of these evidently is the most, the last the least rigid within this temperature range.

In the 45 per cent clay series the lowest viscosity (greatest degree of softening) at the maximum temperature appears with 35 and 40 per cent feldspar, the least with 30 and 50 per cent. The body containing 55 per cent of feldspar is in the intermediate position as far as this point is concerned. The greatest degree of early softening is shown by Nos. 12 and 14. The most rigid body up to 1345° is No. 11, and hence it would appear to be the safest as far as deformation is concerned, within the temperature range indicated. A shorter zone of zero deformation increase is shown by Nos. 12 and 14. The three viscosity stages mentioned above are again noted in this series. Between about 1300 and 1345° three classes of bodies may be observed, namely, those of minimum viscosity, Nos. 11 and 13, of intermediate viscosity, No. 10, and greatest viscosity, Nos. 12 and 14.

The far-reaching effect of higher clay content is at once noted in the 50 per cent clay series. At 1380° Nos. 15, 16, and 17 reach the greatest degree of softening corresponding to an elongation of 1.2 per cent, which is very much less than the maximum value for the other series. The system, therefore, by the further addition of clay has become as a whole very much more rigid. The smaller degree of softening is shown by Nos. 15 and 18. The body containing 50 per cent feldspar is decidedly more viscous than the others containing flint. These two bodies and No. 13 are the ones showing least deformation of the entire series of 18 bodies. We again note the three viscosity stages observed in the preceding series and two classes of bodies, Nos. 15 and 18, and 16 and 17.

Collecting the bodies showing the greatest rigidity or viscosity at 1345°, we have the following compositions:

Number	Clay	Feldspar	Flint
	Per cent.	Per cent.	Per cent.
6	40	30	30
11	45	35	20
13	45	50	5
15	50	30	20
18	50	50	.....

SUMMARY.

Throughout these series the effect of higher feldspar content was to increase viscosity in a very marked degree, especially in the case of the low clay bodies. This is shown by a comparison of the elongation observed in the first paper published, using a load of 5 pounds per square inch, with that observed in the present work, employing a load of 14.5 pounds per square inch. Thus a body with 40 per cent clay and 25 per cent feldspar under a stress of 5 pounds per square inch showed at 1310° an elongation of 7.62 per cent, while one with 40 per cent clay and 30 per cent feldspar, with a load of 14.5 pounds per square inch, resulted at 1315° in an elongation of only 0.8 per cent, indicating a viscosity about 11.8 times as great. A slight decrease in viscosity is noted in the 40 per cent clay series when all of the flint is replaced by feldspar. With 45 per cent clay, 35 and 40 per cent of feldspar are most effective in decreasing the viscosity, but higher percentages again increase it. A still higher clay content causes the softening effect of the feldspar to diminish decidedly. Flint in such high feldspar bodies does not seem to be an important factor in governing the viscosity. The greatest rigidity is evidently due to the large clay content, and hence for high temperature porcelains high clay content is essential.

The function of viscosity is not a continuous one. After attaining a certain degree of softening a well-defined rigid state ensues which does not tend to approach further softening until a temperature of 1345° has been reached. Beyond this point the second stage of decided softening is entered upon. Although showing the same degree of viscosity at 1388°, bodies may be divided into several classes, according to the degree of softening observed between about 1300° and 1345°, which seems to be the most useful criterion. High clay bodies having feldspar as the only other constituent show very great viscosity. The most viscous bodies have been assembled.

The results should be of some service in the selection of bodies least subject to deformation in the firing process.

WASHINGTON, June 15, 1915.

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S. W. STRATTON, DIRECTOR

No. 51

USE OF SODIUM SALTS IN THE PURIFICATION OF CLAYS AND IN THE CASTING PROCESS

BY

A. V. BLEININGER, Ceramic Chemist

Bureau of Standards

[ISSUED SEPTEMBER 25, 1915]

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USE OF SODIUM SALTS IN THE PURIFICATION OF CLAYS AND IN THE CASTING PROCESS

By A. V. Bleininger

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I. INTRODUCTION

Clays suspended in water are affected by the presence of small amounts of electrolytes to a remarkable extent. Alkalies tend to hold the clay in suspension in a fine-grained and jellylike mass

(state of deflocculation); acids and salts operate to coagulate and precipitate the material, leaving a clear supernatant solution (state of flocculation). The viscosity of the clay-water system may also be caused to change so that a constant degree of fluidity can be maintained with a low water content by the use of alkaline substances and with a high water content by the addition of acids and salts. The changes in the viscosity of the system make possible the employment of such a process for accomplishing definite industrial objects.

Clays consist of a more or less heterogeneous collection of coarser and finer mineral particles, varying in specific gravity, size, and shape.

The particles of the clay substance proper may be estimated to have a mean diameter of about 0.005 mm with grains possibly as large as 0.01 mm and some so small as to become submicroscopic. Zsigmondy [1] estimates the mean length of kaolin particles to be 0.003 mm. Using the elutriating apparatus, a velocity of the water current of 0.18 mm per second is supposed to remove all of the clay substance. The nonplastic portion of the clay is, as a rule, considerably coarser, though not always, as it is quite possible to have present quartz, ferric oxide, and other minerals in an extremely fine state. The action of the electrolytes concerns chiefly the very finest material and decreases in effectiveness with the size of the particles.

It may be possible, by lowering the viscosity of the clay-water suspension, to bring about a more or less complete separation of the slightly coarser and heavier grains from the more finely dispersed matter, a differentiation which would not be possible without the use of the alkaline reagent. Again, since the principal impurities, the iron-carrying minerals, and the quartz are essentially coarser grained than the clay substance proper, such a procedure would render the elimination of these substances feasible, and hence points out a way toward purifying the kaolins, which constitute the basis of all white ware and porcelain. The principal objection to the use of American kaolins has been the claim that they are not as pure as the corresponding European materials.

[1] Zur Erkenntniss der Kolloide.

It would seem, therefore, a matter of sufficient economic importance to study the effects brought about by the use of alkaline salts in the washing process.

The casting process consists in shaping clay articles of all shapes and sizes by pouring a thick water suspension of the body ingredients (slip) into plaster of Paris molds. The porous plaster at once begins to absorb water from the slip and a coating of the clay body forms on the surface of the mold. After a sufficient length of time has elapsed, depending upon the thickness of wall desired, the remaining slip is poured off, leaving the required shape of the article within the mold. Upon partial drying, the clay body stiffens and shrinks away from the mold so that the piece can be removed and drying completed. By making up a body mixture into a slip with pure water, the resulting shrinkage of the cast piece would be very high, and in the case of heavy articles considerable loss due to checking and cracking would be caused. By the addition of alkaline compounds, usually a mixture of sodium carbonate and sodium silicate, the amount of water required is decreased very greatly and with it the drying shrinkage. The sodium salts, therefore, are necessary for successful casting.

The effect of the alkaline reagents is complex in character and varies with the nature of the clay and the amount of salts added. Increasing proportions of the alkali usually bring about increasing suspension of the fine particles, a condition which reaches a well-defined maximum—complete deflocculation. Further additions tend to reverse the equilibrium and the material is precipitated or coagulated. This may again be followed by another deflocculation phase. Clays carrying soluble salts, like calcium or magnesium sulphate, do not respond readily to the alkaline reagents, because of reaction between the sulphate and the sodium salt.

The present work was undertaken for the purpose of studying the effect of the alkalies upon the behavior of clay suspensions, embracing the materials commonly used in the manufacture of the finer clay products, with special reference to the purification of clays and the casting process.

II. EFFECT OF ALKALIES UPON THE SEDIMENTATION OF CLAYS

1. GENERAL PRINCIPLES

The deflocculating effect of alkali additions to clays may be observed visually by the change in the appearance of the suspension, the holding up of cloudy masses of the material and also by the determination of the viscosity of the clay-water system. Deflocculation corresponds to decreasing viscosity and the maximum stage coincides with minimum viscosity.

The differences obtaining between the conditions of the settling of clay in water and in such an alkaline solution may be readily illustrated by placing equal amounts of the same kaolin in two glass tubes and adding to one ordinary water and to the other the same volume of a solution carrying the proper amount of alkali required to bring about complete deflocculation. In the tube containing the water, sedimentation of the coarser particles will be observed, but the amount of coarser material thrown down will be less than in the case of the alkaline solution. Likewise, the precipitated granular matter, in the case of the water, will be found to contain more or less fine clay matter carried down mechanically, while the alkaline solution brings about a clean, sharp separation between the two kinds of material.

Again, while the clay-water suspension may still carry particles of iron-carrying minerals, like larger flakes of biotite mica, these have been settled in the deflocculating solution.

By comparing a drop of the alkaline suspension under the microscope with a drop of the ordinary water slip the former will be found to contain a far greater number of particles showing Brownian movement. Evidently the alkali has been active in increasing the dispersion of the clay substance. Upon adding to the alkaline suspension an amount of acid greater than that required for neutralization coagulation will take place. The cloudy mass will be precipitated to the bottom of the tube and the supernatant solution will appear clear. The Brownian movement of the particles will have diminished greatly because of their larger size.

The prompt settling of the granular particles brought about by the decreased viscosity of the system is explained by the fundamental relation expressed by Stoke's law

$$v = \frac{2\ r^2\ g}{9\ k}(d - d_1)$$

where v = velocity of settling, r = radius of particles, k = viscosity, d_1 = density of fluid, d = density of particles, and g = gravity constant, in which the viscosity factor is evidently of prime importance.

The physical changes of the suspension are quite complex, however, for if dispersion is the principal function involved, it must be assumed that the fine grains of clay already present should be still further subdivided into submicroscopic particles, resulting in a certain amount of lyophile, emulsoidlike substance. Indeed, by filtering an alkaline clay suspension through paper such a material may be separated. This pseudoemulsoid may play an important part in such a suspension, tending to prevent further decrease in viscosity and to hold up fine particles which otherwise might tend to settle.

It is quite well understood by this time that the "liquefying" action of the alkaline salts, sodium carbonate, and sodium silicate upon clay is due to the action of the OH' ions present in the solution. Both sodium carbonate and sodium silicate are strongly hydrolyzed, containing an excess of hydroxyl ions, according to the state of the equilibrium, the temperature, and the extent to which the Na ions are absorbed. Sodium carbonate in solution is completely ionized into 2 $Na^{\cdot}$ and CO_3'' ions, and these react with the OH' and the $H^{\cdot}$ of water to form sodium hydroxide and carbonic acid, respectively. Similar hydrolysis occurs with the sodium silicate. The negatively charged OH' ions repel the similarly charged clay particles electrostatically. Repulsion may take place only when the electrical charges of the particles are approximately equal. This increases the state of dispersion of the system, breaking up the larger particles into smaller ones. Hence the water penetrates more deeply into the clay structure and causes the clay to "liquefy." The maximum amount of deflocculation is brought about by a definite concentration of OH' ions, and if

exceeded, "stiffening" will again take place, during which period the alkalinity decreases. This stage may again be followed by a second liquefaction, due to absorption of the salts. Organic colloids appear to act somewhat similarly to the sodium salts in bringing about increased dispersion; but at the same time the latter seem to protect the particles against flocculating cations, so that the suspension is less sensitive to the action of coagulating salts. The alkaline, fluid, casting slip without the presence of sufficient amounts of organic colloids is at once changed to the stiffened condition by the introduction of salts like the sulphates or chlorides of calcium, magnesium, or aluminum. The presence of such salts in the clays, therefore, requires not only an increased amount of alkali to bring about deflocculation, but may even render the maximum liquefaction impossible.

2. USE OF ALKALINE COMPOUNDS IN THE WASHING OF CLAY

The principal impurities in clay are the minerals, quartz, feldspar, siderite, pyrite, ilmenite, biotite mica, and ferric oxide. The first five usually occur in granular form, while the biotite mica is found in flakes more difficult to separate; the ferric oxide, usually hydrated, may be present entirely as a colloid. The last impurity, especially in the case of very fine-grained clays, offers the greatest difficulty in separation, and the task quite often is hopeless, owing to the fact that this material becomes part of the colloidal structure of the clay itself.

In employing alkaline reagents in the washing of clay the process employed need not conflict with the ordinary washing process as now practiced.

The clay material would be blunged up as is now being done, but in place of the water there would be used a very dilute solution of caustic soda or of sodium carbonate and sodium silicate (water glass), in equal parts. The amount of soda in this solution should correspond to the amount required to bring about complete deflocculation. The amount of reagents to be added depends upon the percentage of yield and the character of the clay. The quantity necessary can be determined, however, with sufficient accuracy, so that for each ton of crude clay a definite amount of the alkali compound can be added. After the slip has

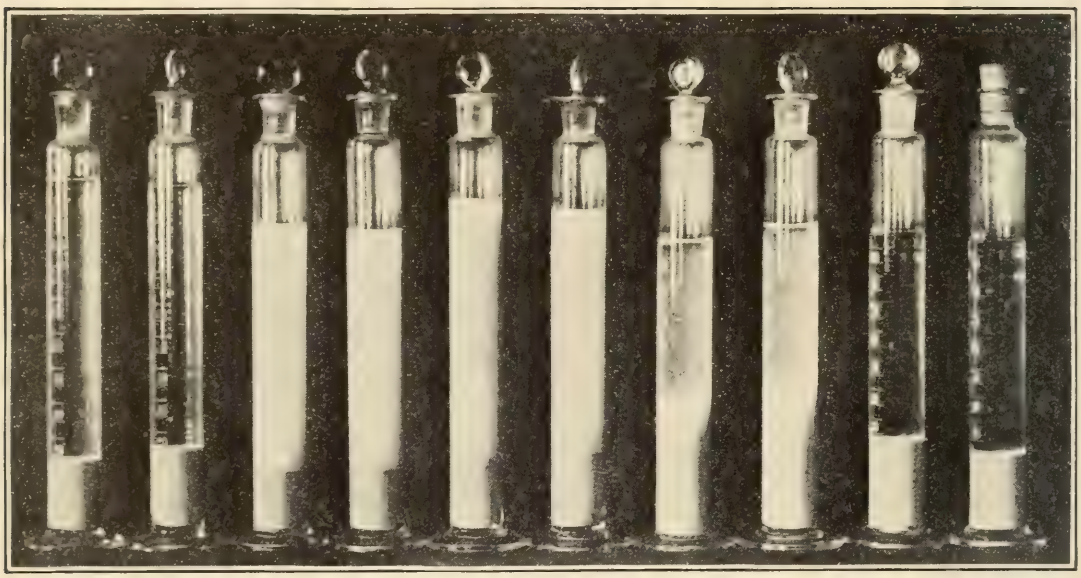

FIG. 1.—*Effect of increasing amounts of NaOH in bringing about deflocculation and reflocculation*

passed through the settling troughs and has been screened and collected in the settling tank it is allowed to stand.

The finer impurities—fine grains of silica, biotite mica, etc.—will now settle. The time of settling governs the degree of purification attained. Longer standing naturally precipitates more of this material than short standing. After a sufficient period the slip is now run into another tank where it is coagulated for the purpose of filter pressing, because the alkaline condition, with the accompanying degree of dispersion into exceedingly fine particles, would tend to clog the filter cloth, and also would cause the press water to run off turbid. At the same time the efficiency of the process would be greatly decreased on account of the slowness of filtration. In the second tank the coagulating reagent, usually aluminum sulphate, is introduced, whereupon the clay will settle out in a curdled mass, which is pumped to the filter press. This precipitation can not be carried on in the first settling tank for the obvious reason that the coagulated clay would mix with the imputities which have been settled out.

The amount of alkaline reagent to be used depends upon the character of the clay. In the materials investigated so far in this laboratory the amounts varied from about 0.05 to 0.2 per cent, or from 1 to 4 pounds per ton of dried clay. The actual cost of the reagent, therefore, should be trifling and should not exceed 7 to 8 cents per ton, including the cost of the aluminum sulphate used for coagulation. Too great an addition might entirely nullify the action. It is important, therefore, that in each case the proper amount of alkali be determined by the use of the viscosimeter, or by means of a series of glass settling tubes in which the degree of deflocculation is readily observed. In Fig. 1 the effect of increasing amounts of caustic soda upon fuller's earth is shown, representing the phases of coagulation, deflocculation, and again of coagulation after standing for 12 hours.

In rare cases, as with certain Missouri fire clays, sodium oxalate has been found to be more effective than the alkaline compounds mentioned above, but the method of procedure is the same.

It is evident from the nature of the process that the greater purity of the clay is obtained at the expense of an increased amount of residue or waste, a fact which must be taken into con-

sideration in the commercial application of such a process. So far the writer knows of only one American washing plant making successful use of the principles involved here, and our own work is based on experiments carried on in the laboratory and with comparatively small amounts of material. It would seem, therefore, that experiments should be conducted on a larger scale. This laboratory would be pleased to be of assistance in helping to carry out such work on a commercial scale.

III. RESULTS OBTAINED IN TREATING SEVERAL CLAYS

1. GEORGIA KAOLIN

It was thought desirable to subject some commercial clays used in the pottery industry to the process here described in order to determine the difference between the treated and the untreated materials. These clays, with the exception of the ball clay, had been previously washed by the customary process and represented commercial shipments.

Porcelain bodies in which the clay substance was partly introduced, as a certain brand of Georgia kaolin, were found to contain particles of impurities which were very objectionable. It was also known that the same clay had been giving trouble in one pottery because of the introduction of black specks. Some shipments of the kaolin were more objectionable for this reason than others, the washing process employed at the mine in question being somewhat erratic.

A 25-pound sample of the Georgia kaolin was taken from stock and blunged in a large ball mill for several hours. Portions of the slip were placed in 500-cc bottles and caustic soda in amounts varying from 0.05 per cent to 0.25 per cent was added to the respective bottles. The bottles were thoroughly shaken and allowed to stand for one-half hour. In this way it was determined that an addition of 0.17 per cent of caustic soda produced dispersion such that the clay slip attained maximum fluidity and an accompanying rapid settling out of the coarser particles.

The slip was placed in a large stoneware jar, 0.17 per cent of caustic soda by weight added, and the slip thoroughly stirred. After allowing to settle for one-half hour the material in suspension was siphoned off, passed through a 150-mesh sieve, aluminum

chloride added, and the flocculated material filter-pressed. Disks 10 cm in diameter were made by pressing the rewashed kaolin in plaster molds. For purposes of comparison disks were also prepared from the kaolin as received from the clay dealers. Bodies having a composition of 50 per cent clay, 30 per cent flint, and 20 per cent spar were made up from the kaolin and the unwashed material and molded into 10-cm disks.

The test pieces molded from the kaolin and from the bodies were fired, unglazed, to cone 10 in closed saggers. The test pieces molded from the rewashed kaolin and the body containing the rewashed kaolin were markedly superior in color and freedom from specks to those molded from the kaolin taken from stock and not rewashed.

2. NORTH CAROLINA KAOLIN

The deflocculation tests on Georgia kaolin were duplicated on a sample of North Carolina kaolin taken from stock in the same manner, the quantity of caustic soda necessary to produce the desired dispersion being about 0.19 per cent. Test pieces were molded as before and fired to cone 10. The North Carolina kaolins appear to respond more quickly to the action of the alkali, the coarser material settling out rapidly.

Although the North Carolina kaolin produced a whiter color than the Georgia and contained fewer particles of dark-burning impurities, a noticeable improvement in color and cleanness was evident in the test pieces molded from the rewashed material.

3. FLORIDA KAOLIN

Florida kaolin appears to respond less readily to the action of the alkali than either the Georgia or North Carolina kaolins. The deflocculation tests were conducted as before on a sample purchased on the market. The amount of alkali added was 0.14 per cent, but some difficulty was experienced in determining just what quantity to use. The Florida kaolin usually produces a very good white color, although sometimes it may contain dark-colored impurities which produce objectionable specks in the finished piece.

The test pieces produced from the rewashed kaolin and fired to cone 10 were slightly improved in color and were markedly free from the black specks brought out in the test pieces molded from the clay as received from the dealer and without rewashing.

4. TENNESSEE BALL CLAY NO. 3

In addition to the characteristic cream or buff color produced in the burning of ball clays, dark-colored specks, due to the presence of particles of impurities, are in evidence. On account of the great plasticity and the consequent difficulty of washing, ball clays are placed on the market in the crude state. In addition the washing of ball clays is discouraged, owing to the supposed decrease in plasticity accompanying the washing process.

The washing tests on the Tennessee No. 3 ball clay were conducted in a manner somewhat different from that for the kaolins. The ball clay was ground, screened, and blunged in a ball mill for a short time. To the mill charge 0.4 per cent by weight of hydrochloric acid was added and the blunging continued for several hours. The slip was placed in a stoneware jar and allowed to settle. The supernatant liquid was then siphoned off and discarded and the clay again blunged with a supply of fresh water, to which was added 0.15 per cent by weight of caustic soda. After standing for one hour the suspended matter was siphoned off, flocculated by an addition of aluminum chloride, and filter-pressed.

A number of 10-cm disks were molded from bodies composed of 50 per cent ball clay, 30 per cent flint, and 20 per cent feldspar, the washed ball clay being used for one body and the crude ball clay for another. The disks were fired to cone 9 in closed saggers.

The body prepared from the washed ball clay, although showing the characteristic buff color of this type of clay, was much improved as regards cleanness of color and freedom from specks of iron-bearing minerals. The buff color was also slightly lightened in the bodies prepared from the rewashed clay.

Means of measuring the increase or decrease in plasticity of the washed ball clay were not at hand, although so far as could be observed from the working qualities of the two materials there was but small difference in plasticity.

5. GENERAL EFFECT OF DEFLOCCULATION UPON COLOR

Obviously in most cases the degree to which the color and general appearance of a clay is improved by the employment of deflocculating agents is a factor of the original purity of the clay and the excellence of the washing treatment to which it is submitted at the washing plant. Clays occur, however, which, although of poor color, can not be improved by the employment of deflocculating agents on account of their physical constitution.

Washing tests on samples of English kaolins to which deflocculants were added did not produce noticeable improvement in color, owing to the original purity of the materials or the excellence of the washing treatment. Of the three varieties of American kaolins subjected to the deflocculating treatment, as stated before, the Georgia kaolin showed the greatest improvement as regards color. The improvement in the North Carolina and Florida kaolins was not so noticeable, although the gain was well worth the expense of the treatment.

6. EFFECT UPON DRYING AND BURNING SHRINKAGES

The drying and burning shrinkages of the kaolins and bodies are affected somewhat by the use of deflocculating agents. The average shrinkage measurements in the following table were made upon 10-cm disks, which were prepared from the kaolins and bodies by pressing in plaster molds. The disks were dried at 110° C and fired in saggers to cone 10.

TABLE 1

Shrinkages (in percentages of dry length) Cone 10

Kaolins	100 per cent clay		50 per cent clay, 30 per cent flint, and 20 per cent feldspar	
	Drying shrinkage	Burning shrinkage	Drying shrinkage	Burning shrinkage
Florida kaolin, as received	7.55	12.45	5.45	7.90
Florida kaolin, washed	7.30	12.70	4.75	9.15
North Carolina kaolin, as received	4.75	5.40	3.05	7.40
North Carolina kaolin, washed	3.70	6.92	2.20	8.75
Georgia kaolin, as received	4.60	12.75	4.05	9.45
Georgia kaolin, washed	3.90	15.20	2.60	9.10

It will be noted that the addition of the alkali caused a decrease in the drying shrinkages of the test pieces containing the kaolins which were subjected to the washing treatment. This decrease is most noticeable in the body containing the washed Georgia kaolin.

Treating the kaolins with the electrolyte, however, increases the burning shrinkage of the test pieces, with the exception of the body containing the Georgia kaolin. This increase in burning shrinkage is due to the removal of the fine-grained, nonplastic materials from the kaolins and the presence of a proportionately greater amount of clay substance.

IV. ELECTRICAL SEPARATION OF CLAY

1. GENERAL DESCRIPTION

A new electrical process for the purification of clay, invented by Count Schwerin,[2] in Germany, is causing widespread interest. The treatment consists in stirring up the clay with water and removing the coarse material by means of screens and settling. A previously determined amount of electrolyte is added and the suspension conveyed to the osmosis apparatus, which is in the form of an endless metallic belt upon which the purified clay is deposited. The clay is scraped off and conveyed to the dryers. It is claimed that the product contains only 25 per cent of water and is free from pyrites, sand, or other impurities, has a lower alkali and higher alumina content, and is greatly improved in color, plasticity, bonding power, refractoriness, and uniformity.

It was thought desirable to examine the principle under which this process operates, and to carry on a few experiments intended to bring out more clearly some of the factors involved.

2. THEORY OF PROCESS

Small particles in suspension between two electrodes will move under the influence of a direct current either to the cathode or the anode. This phenomenon is called kataphoresis. Suspended particles of shellac, clay, quartz, cotton, silk, starch, graphite, sulphur, etc., travel to the positive electrode. The suspended

[2] Tonindustrie Zeitung, **36**, pp. 1283–1285; Trans. English Cer. Soc., **12**, Part I, pp. 36–65.

particles are always electrically charged and, according to the + or − character and the magnitude of the charge, they migrate to the negative or the positive pole. In pure water most substances are charged negatively. Water itself is positive in electroendosmosis and moves toward the negative pole. No electro-osmotic effects are noted in liquids like chloroform, ether, petroleum, oil of turpentine, etc. The addition of very small quantities of electrolytes to solutions used in kataphoresis may promote endosmosis or oppose it. Larger additions of any electrolyte cause the action to cease entirely. According to Freundlich [3] "it is to be expected that the addition of OH′ ions to a negatively charged particle would raise the kataphoretic migration velocity to the positive pole, while acids and cations of higher valency would decrease it with increasing concentration, reduce its value to zero, and finally change its sign With small particles, positively charged, the OH′ ion and the anions of higher valency are active in the same direction." Clay containing a considerable content of soluble salts should therefore be expected to respond poorly. Whitney and Blake [4] found that upon adding 0.004 normal nitric acid solution to colloidal silver the particles originally migrating to the positive pole reversed their direction. A similar reversion was shown upon the addition of aluminum sulphate.

It is evident that the effect of the additions of electrolytes is intimately connected with the flocculating action of the salts.

The velocity of migration of fine particles seems to be independent of their size and shape within certain limits. It is interesting to note that this velocity does not differ considerably from the value given for the more inert ions like sodium. While for the latter the velocity constant is 43×10^{-5} cm per second, for a drop in potential of 1 volt per centimeter, the velocity of quartz particles, averaging 0.001 mm in diameter, is 30×10^{-5} cm under the same conditions. There appears to be no direct relation between the amount of clay separated and the current used, and the separation is hence not governed by Faraday's law.

[3] Kapillarchemie, p. 239.

[4] Jour. Am. Chem. Soc., 26, p. 1339.

3. STAGES OF ELECTRICAL SEPARATION

The process of electrical purification may be said to consist of three operations—the blunging and screening of the clay, the treatment with electrolyte, and the separation upon the positive electrode. It is evident that the washing process in itself accomplishes a great deal in removing impurities such as sand, feldspar, pyrites, etc. To afford strict comparison between the washing process and electrical purification it is not fair to compare the crude with the electrically treated material. The difference between the washed clay and that treated by the new process must be used to establish the merits of the case.

The additional separation brought about by the use of an electrolyte is really the most important factor in the scheme. By the proper treatment with small amounts of chemicals the viscosity of the slip may be decreased so that considerable quartz and feldspar, ordinarily held in suspension, may be thrown down. The suspended material thus remaining is of course of greater purity, and the deposit attached to the electrode should therefore be clay of better grade than that which is obtained by the ordinary washing, as has been shown in previous paragraphs.

It is obvious that the same treatment can be applied where the slip is to go through a filter press, there being needed only adequate tank facilities for the separation of the suspended matter. The electrical treatment itself has very little to do with the purification, since the coarser impurities have already been removed by the previous precipitation treatment. The manner of deposition upon the electrode is of a mechanical character and takes the place of filter-pressing, having of course the advantage of being continuous and automatic. Other methods of separating the clay from the water might be employed, such as the Sweetland system of filter-pressing, the economy of which should approach ideal conditions.

4. RESULTS OF ELECTRICAL SEPARATION EXPERIMENTS

In the present work it was thought advisable to collect further information (1) in regard to the reagents most suitable for the treatment preliminary to the actual separation and the determi-

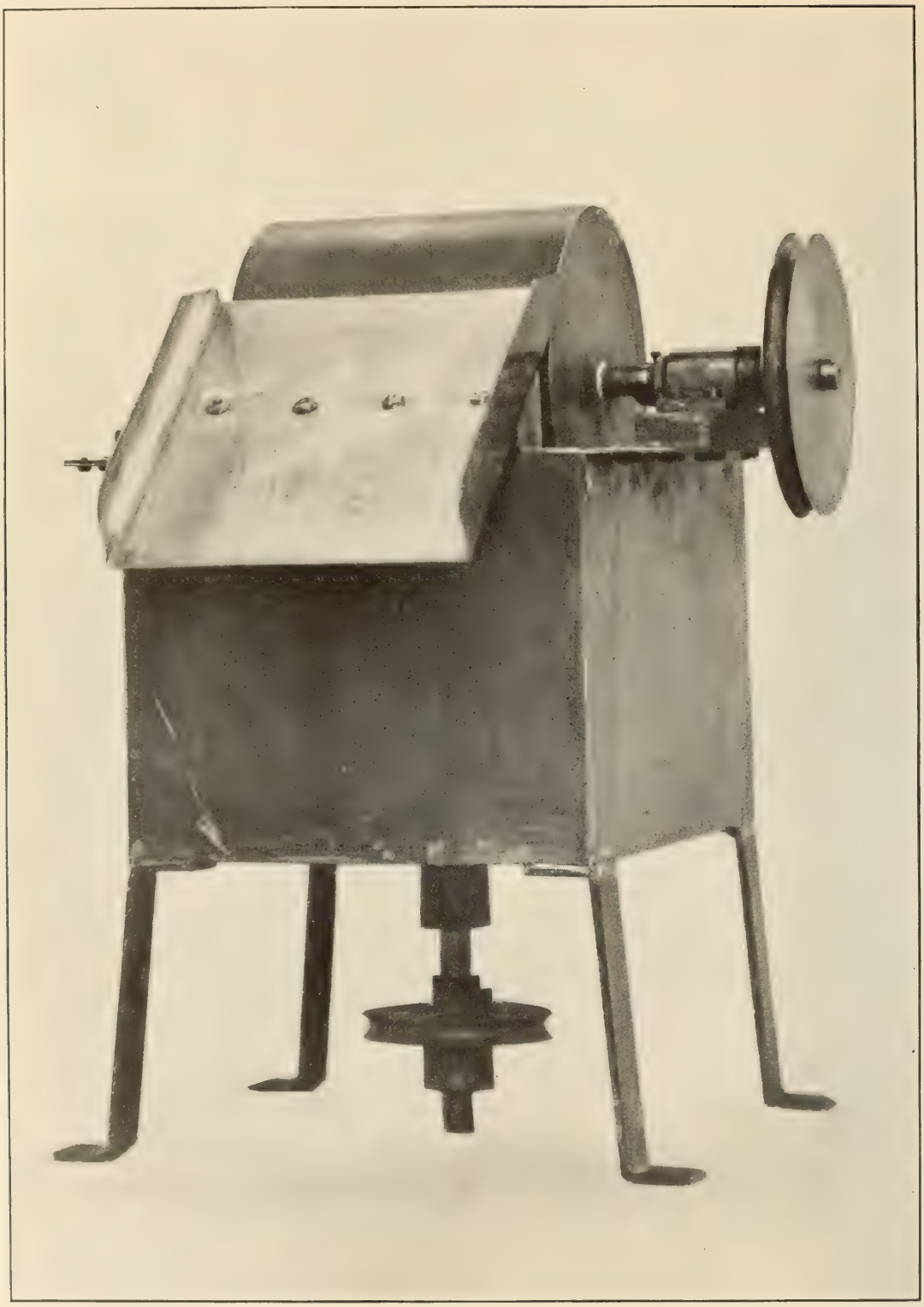

FIG. 2.—*View of electrical separating apparatus*

nation of the proper amount to be used; (2) in regard to the behavior of different materials such as quartz, feldspar, ferric oxide, and several types of clay when subjected to the electrical treatment.

It was found, in agreement with Ashley's work,[5] that sodium hydroxide and sodium oxalate are the most effective reagents, the former to be used in the majority of cases, while the second substance is particularly suitable in the case of certain fire clays. For the purpose of determining the proper amount of the reagent, viscosity determinations by means of the efflux tube were found most convenient. The method of procedure was to add small quantities of NaOH to the slip, making viscosity readings until the minimum point of the curve was reached. This consistency proved to be the most suitable for the electrical separation. In cases where the sodium hydroxide was found to be less effective resort was had to the use of sodium oxalate, $Na_2C_2O_4$. In this simple manner the proper conditions are readily obtained. Indiscriminate additions of chemicals will lead to misleading results and unsatisfactory separation. The amount of the reagent necessary is small and never exceeds 0.2 per cent in terms of the dry weight of the clay. An excess of the reagent must be avoided in all cases.

The work dealing with the electrical separation of suspended materials was mostly done by means of a very simple apparatus. A 220-volt direct current was available, controlled by two water rheostats. The separating receptacle was a copper can 6 inches in diameter and 5 inches high. This was filled with the slip, and a flat carbon electrode was just immersed. Electrical connections were made with the can and electrode. The latter was a carbon plate of which there was a stock on hand. In the commercial apparatus it is said that the positive electrode consists of type metal, though aluminum or other metals may be used. By means of a volt and ammeter the current was under observation.

For handling larger quantities of material an automatic apparatus was built (Fig. 2) consisting of a copper tank 5¾ by 6½ by 7¼ inches, in which a revolving drum 5 inches in diameter and 4¾ inches wide, insulated from the tank, was used as the positive

[5] Bureau of Standards, Technologic Paper No. 23.

electrode. The negative electrode consisted of two insulated metallic strips beneath the roll. The clay adhering to the surface of the drum was scraped off at the opposite side. A slow-moving stirrer was also provided at the bottom of the tank to prevent undue separation. A flush hole was arranged for washing out the residue after each run.

In the following paragraphs the results obtained in the electrical separation of several materials are described.

Flint.—Finely ground flint was found to separate well, forming a dense layer at the positive electrode with voltages varying between 125 to 180 and a current strength of 0.75 ampere. With this material the deposition upon the electrode was most satisfactory without the addition of any electrolyte.

Feldspar.—With a sample of Brandywine feldspar, which was rather coarsely ground, practically no separation took place with or without electrolyte. Using Maine feldspar deposition occurred, but not as marked as with the flint. The voltage used was 160, with 0.75 ampere. The addition of electrolytes produced no increase in yield.

Ferric Oxide.—Finely divided ferric oxide in suspension formed no deposit with or without electrolyte. An addition of 6 per cent of this oxide was then made to North Carolina kaolin, and the treatment carried out upon this mixture. Upon determining the ferric oxide in the original mixture and in the portion separated on the electrode, it was found that no reduction whatever in the iron content was accomplished. All of the ferric oxide admixed with the kaolin was carried along with the clay particles.

Kaolin.—In order to determine whether further purification could be brought about with washed clays, runs were made with the North Carolina and Florida kaolin. In both cases heavy firm deposits were obtained with a content of 0.2 per cent caustic soda with voltages varying from 80 to 160. Practically all matter in suspension was carried to the electrode. The densest layer is obtained with the highest voltage.

Impure Fire Clay.—A fire clay of the No. 3 type, from Aultman, Ohio, was ground to pass the 40-mesh sieve and made into a slip showing minimum viscosity with 0.1 per cent caustic soda. The separation took place very satisfactorily. Upon making briquettes

from the original clay, the separated portion, and the residue, the linear drying shrinkages were found to be 8.4, 7.5, and 6.25 per cent, respectively. Upon burning the specimens to cone 9 in a sagger the separated portion was decidedly superior in appearance, showing a uniform light-gray color, while both the original clay and the residual part were darker and showed numerous black spots.

In connection with these experiments the reverse effect, that of the negative electrode upon plastic clay, was briefly verified. Upon making a steel trowel the negative pole, it was found that water was drawn from a mass of plastic clay into which the tool was inserted and thus caused the latter to penetrate very readily. This confirms the results reported in a paper before the National Brick Manufacturers' convention of 1912 at Chicago.

5. GENERALIZATION, BASED ON RESULTS OBTAINED

With the general run of clays the suspended clay will be deposited by the electrical current just as it is, and if it has not been subjected to the sedimentation process mentioned the quality of the product will not be superior to that of ordinary washed clay. The desired results can be obtained by the chemical washing process first described with the use of the filter press without resorting to the use of electricity. However, if the electrical continuous separation can replace the filter press economically its use would be justified. At the present time no exact figures are available for purposes of comparison. To a large extent it would be a matter of the comparative economy of the electrical endosmose apparatus and the filter press. If the latter should be improved, as has been done in the so-called clamshell press, it is quite possible that the economic advantage might remain with the filter press.

V. FUNCTION OF THE ALKALIES IN THE CASTING PROCESS

1. VISCOSITY OF SLIPS

The principal effect of the alkaline additions to a casting slip is to decrease the amount of water required to hold unit weight of clay in the suspended state with sufficient fluidity to permit of pouring.

The practical aim in casting evidently must be to increase the weight of clay body carried by unit volume of the water to the maximum. From 29.5 to 30.5 ounces per pint is the usual weight to which casting slips are carried in the case of white vitreous bodies. It is evident that the content of clay and nonplastic additions bring about variations in this respect. At the same time the composition of the body should be of such a nature that proper drainage of the water from the stiffening mass to the mold may occur. The effect of the alkaline reagents added to a slip is followed most readily and quantitatively by the determination of the viscosity. For this purpose various types of flow or torsion viscosimeters may be employed. Owing to the coarse nature of the suspensions the accurate flowtubes of Ostwald are out of the question, and exceedingly simple devices like the brass efflux tubes illustrated in Fig. 3 may be used. Here the time required for a given volume of slip, say 200 cc, to flow through an orifice 5/32 inch in diameter is determined. The effect of the varying head due to the lowering of the level of the liquid is largely overcome by the employment of Mariotte's principle of the immersed tube. It is necessary for the proper working of the device that all joints be made air-tight. By determining the time required for the flow of water at 18° C, and dividing the observed time for the same volume of slip by this constant quantity, the viscosity of the suspension in terms of water is readily computed. For the technical determinations in question, corrections such as are necessary in the use of the Ostwald viscosimeter are not required. It was likewise found that corrections for temperature are negligible.

Of the torsion viscosimeters the Coulomb and Couette instruments are available, while for accurate results expressed in absolute units the Clark viscosimeter renders good service. The Couette apparatus represents probably the most satisfactory one for determining relative viscosity. It consists of a vessel rotating at constant speed, which contains the liquid. A metal cylinder suspended by means of a wire is immersed in the suspension. The torsion exerted upon the wire may be measured by means of a mirror attached to the projection of the cylinder to which the wire

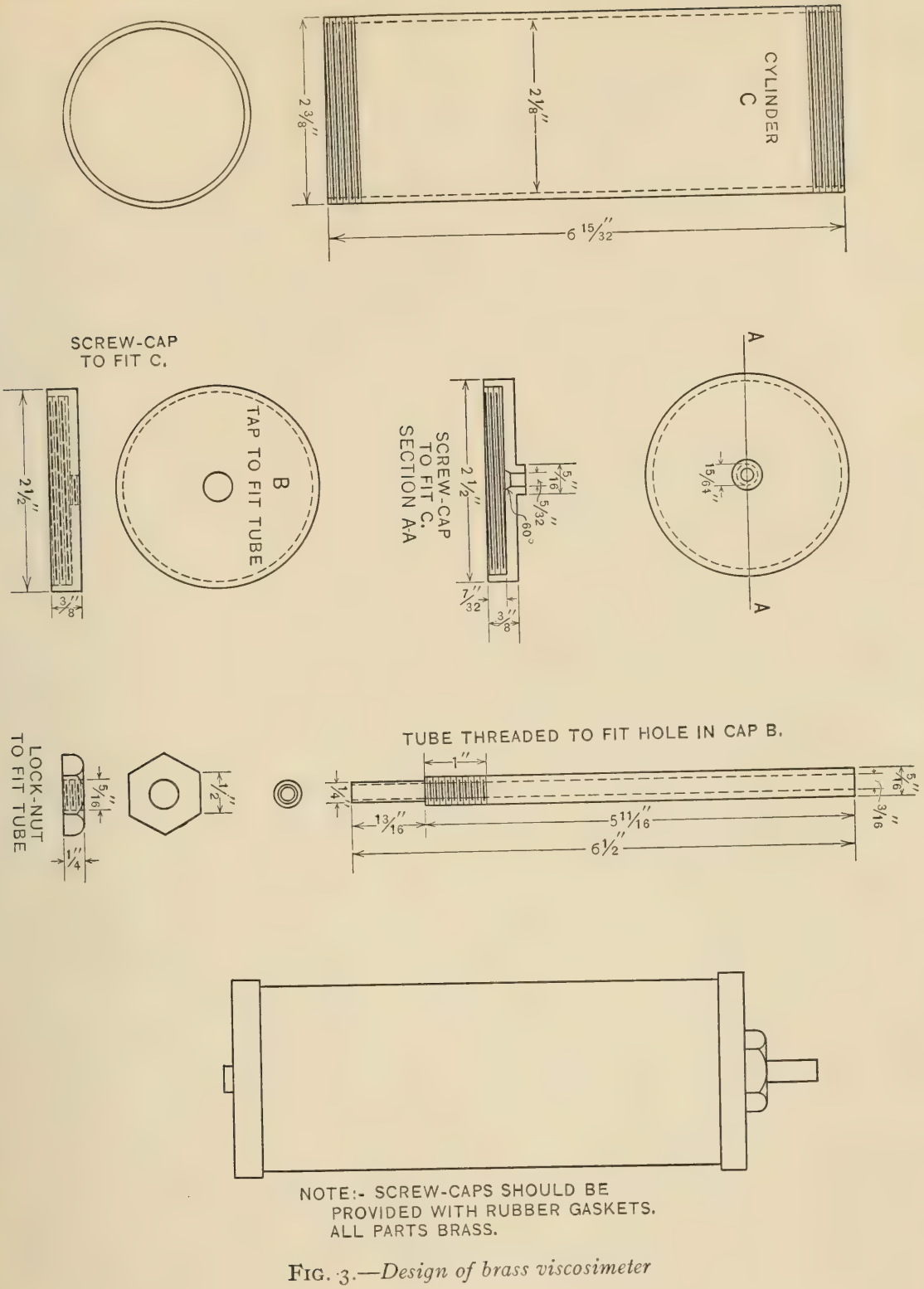

FIG. 3.—*Design of brass viscosimeter*

is attached and the angular deflection noted upon a graduated scale at a suitable distance from the instrument. Various investigators, like Hatschek and others, have found this apparatus very suitable in their investigation of colloids. The flow viscosimeter as used in this work, is sufficiently accurate for purposes of comparison and has the advantage of being simple and cheap.

In the study of dispersed systems of any kind the viscosimeter may be considered as important as the voltmeter and ammeter in the measurement of electrical quantities.

In general, the viscosity of a disperse system may be said to correspond to the relation suggested by Einstein, Hatschek, and others,

$$n_1 = n_2\left(1 + K\frac{v_1}{v}\right)$$

where n_1 = viscosity of the system,

n_2 = viscosity of continuous phase (water in case of clay slip),

v_1 = volume occupied by colloidal particles,

v = total volume,

K = constant.

In many colloidal systems the value of the constant has been found by Hatschek to approximate 4.5 for small concentrations. Owing to the large amount of comparatively coarse material in clay and body suspensions, the Hatschek constant of the above equation can not be expected to hold for systems of this kind, but is certain to vary with the different materials. In the case of Florida kaolin it was found to be 5.05 for small concentrations. Using this relation, it is assumed, of course, that the conditions of the system are practically in equilibrium, as time, temperature, absorption, and other factors are likely to bring about changes in the viscosity without change in the volume relations of dispersing medium and dispersed matter.

The medium which holds up the nonplastic matter in casting slips must be considered to consist of a pseudoemulsion, resulting from the further breaking down of the finer clay particles. It is essential that the viscosity of the slip be maintained sufficiently high by the use of enough clay to prevent separation, which is likely to occur, in agreement with Stoke's law.

It is easy to see that the use of comparatively coarse clays, resulting in an insufficient amount of the emulsoid substance, while draining readily, might give rise to difficulties due to separation. The viscosity of a clay suspension supposedly in equilibrium, and with it all accompanying properties, are not maintained constant. Variations occur with a number of factors, as temperature, time, and change in the concentration of the dissolved salts due to absorption, solution, or reaction. Clays, of course, differ widely also in their response to the action of the alkalies. The physical structure (fineness) of clays and their chemical composition with special reference to the content of soluble salts, cause them to behave differently. The previous mechanical treatment of the clay, as by washing or drying, is also of considerable influence.

2. OUTLINE OF WORK

The present work deals with the following topics:

1. The effect of increasing amounts of Na_2CO_3 and Na_2SiO_3 upon the viscosity of four body slips in which the feldspar and flint are kept constant at 21 and 34 per cent, respectively, and 45 per cent clay is introduced in succession by North Carolina kaolin, Georgia kaolin, Florida kaolin, and Tennessee No. 3 ball clay. The sodium silicate used contained in the dried state 70.3 per cent SiO_2 and 29.7 per cent Na_2O, corresponding to the formula $Na_2O.2.44SiO_2$, which is to be understood when mention is made of sodium silicate throughout this paper.

2. The effect of various proportions of North Carolina kaolin body upon each of the three other bodies, with reference to the viscosity of the resulting mixtures.

3. The absorption of Na_2CO_3 and NaOH by Florida and Georgia kaolins.

4. Tensile strength of bodies cast under different conditions of consistency and viscosity.

5. Calculation of constant in general viscosity formula for different concentrations of Florida clay slips.

6. Effect of time on change of viscosity of casting slips.

VI. EFFECT OF VARIOUS AMOUNTS OF SODIUM CARBONATE AND SODIUM SILICATE

1. NORTH CAROLINA KAOLIN BODY

This mixture was made up to a slip containing 59.73 per cent of solids. The viscosity was determined by means of the efflux tube

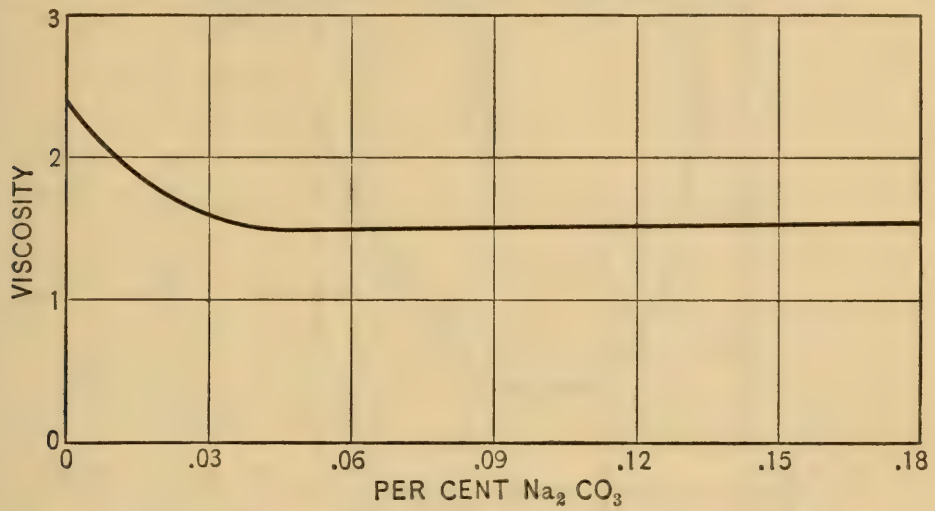

FIG. 4.—*Effect of sodium carbonate on North Carolina kaolin body*

already described. Two series of tests were run, one with increasing amounts of sodium carbonate and one with sodium silicate.

The Na_2CO_3 tests are shown in the diagram of Fig. 4. From

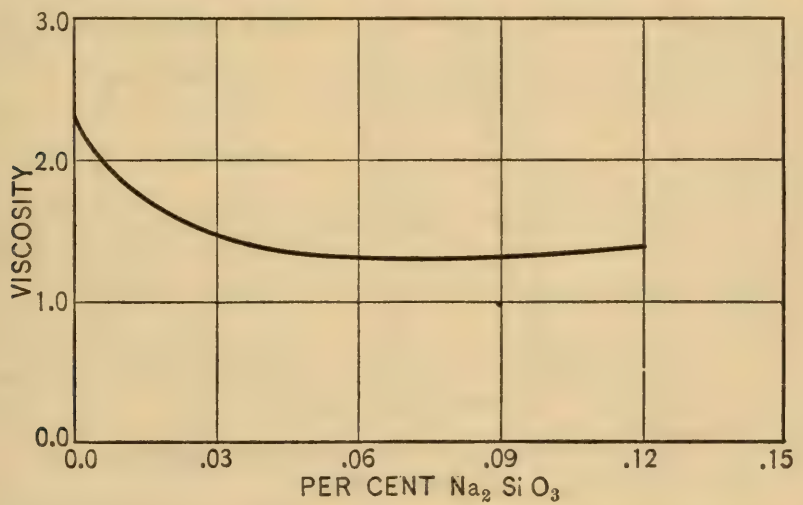

FIG. 5.—*Effect of sodium silicate on North Carolina kaolin body*

this curve it is seen that there is no very large drop in viscosity and that the minimum is reached with 0.045 per cent of the reagent. No tendency toward a maximum point is noted. This illustrates very nicely the deficiency in the amount of pseudo-

emulsoid resulting from the use of this clay, owing to its comparatively coarse nature. Either the amount of highly dispersed material is quite small or all the grains are too coarse to be affected decidedly by the reagent employed.

Sodium Silicate Series.—In this case (Fig. 5) similar conditions

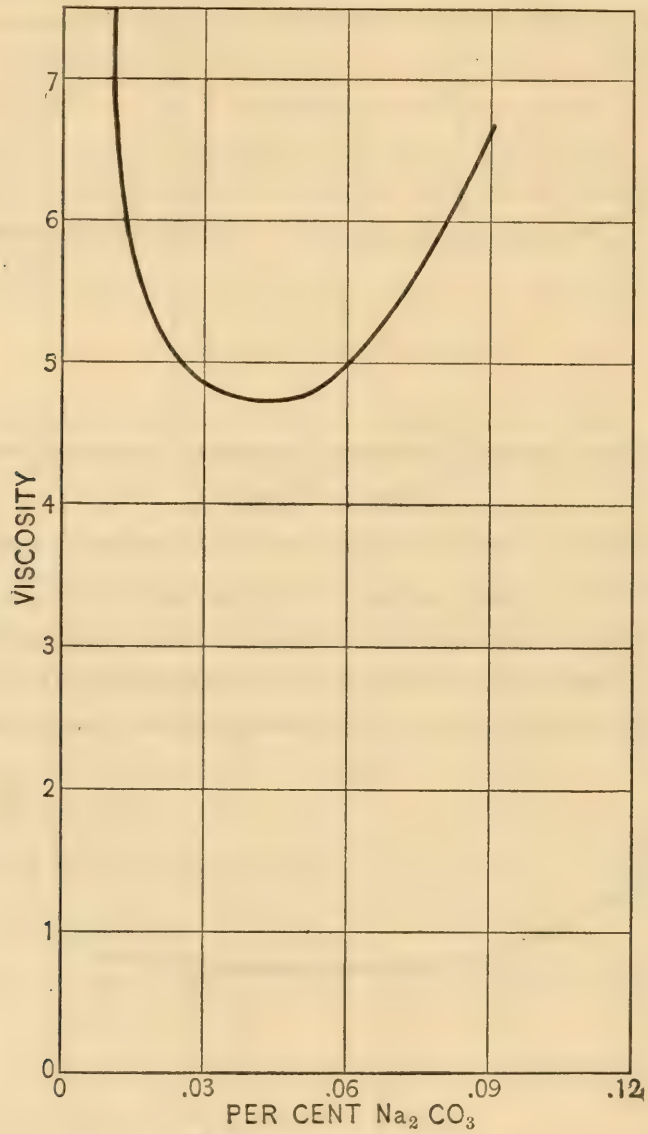

FIG. 6.—*Effect of sodium carbonate on Georgia kaolin body*

prevail and the minimum point is likewise reached with 0.045 per cent. The drop in viscosity is from 2.35 to 1.30. It appears, therefore, that owing to the comparatively coarse dispersion of this kaolin the system is not greatly influenced by the alkali reagents.

2. GEORGIA KAOLIN BODY

Sodium Carbonate Series.—The slip used for both series contained 61.38 per cent solids. From Fig. 6 it appears that the initial viscosity is very much greater than in the case of the North Carolina kaolin body. The value was above 7, but could not be determined accurately owing to the thickness of the slip. A content of 0.03 per cent Na_2CO_3 at once lowered the viscosity to 4.75, reaching a sharply defined minimum. With more than 0.045 per cent of the reagents the viscosity at once increases. This kaolin therefore is very sensitive to changes in the alkali concentration, and hence requires greater care in regard to this point.

Sodium Silicate Series.—In this case (Fig. 7) the minimum viscosity, 2.3, represents a considerably greater drop in viscosity than is the case with the carbonate. This reagent is therefore very much more effective. Although the tendency of the curve toward an increase in viscosity is clearly shown, the change is very much less abrupt than in the first case and the range of minimum viscosity considerably wider.

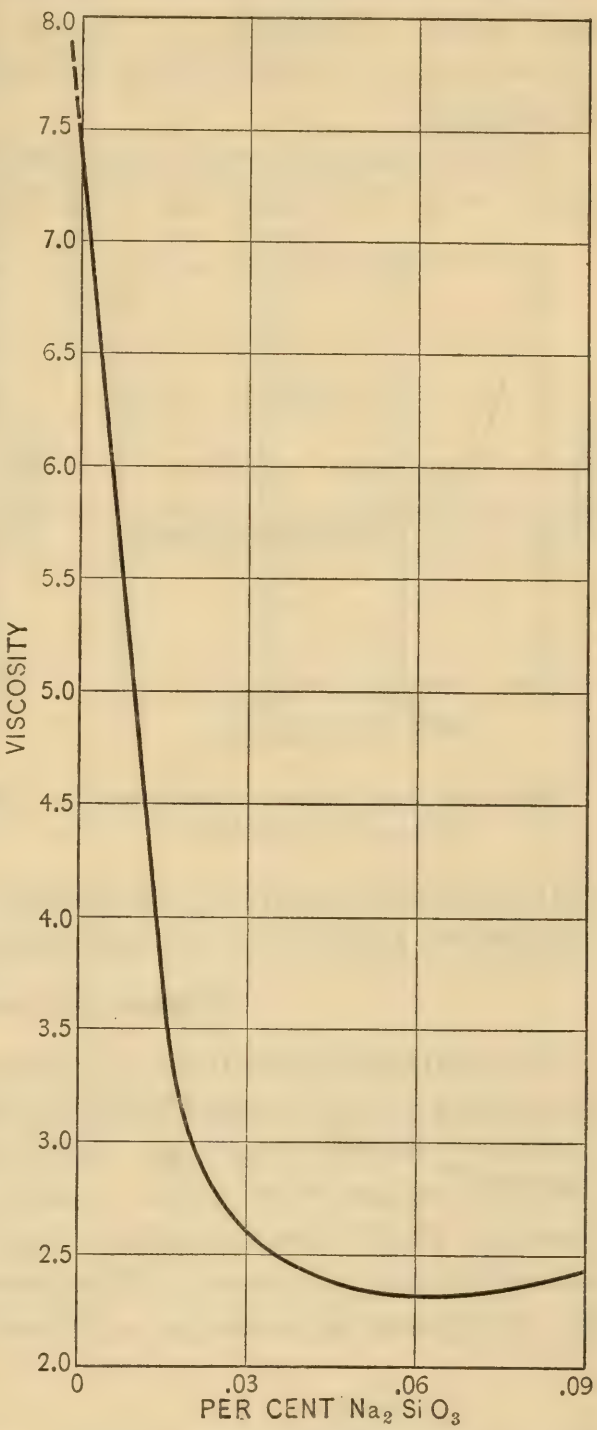

FIG. 7.—*Effect of sodium silicate on Georgia kaolin body*

3. TENNESSEE BALL CLAY BODY

Sodium Carbonate Series.—The slip as used contained 47.68 per cent solids. From Fig. 8 it is seen that the drop in viscosity is 1.9 with 0.03 per cent reagent, and that no well-defined minimum is indicated.

Sodium Silicate Series.—Practically the same results are obtained with this reagent as with Na_2CO_3 (Fig. 9). It is evident

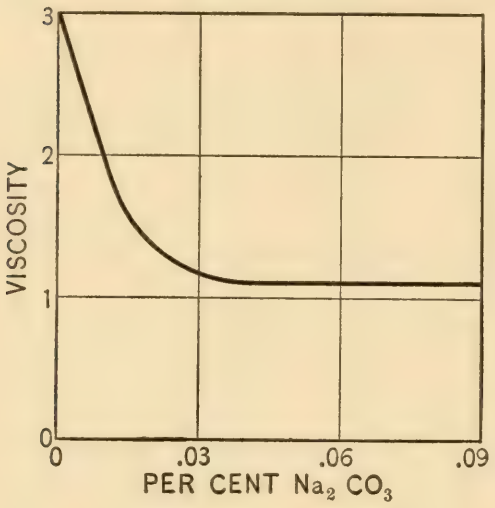

FIG. 8.—*Effect of sodium carbonate on Tennessee ball clay body*

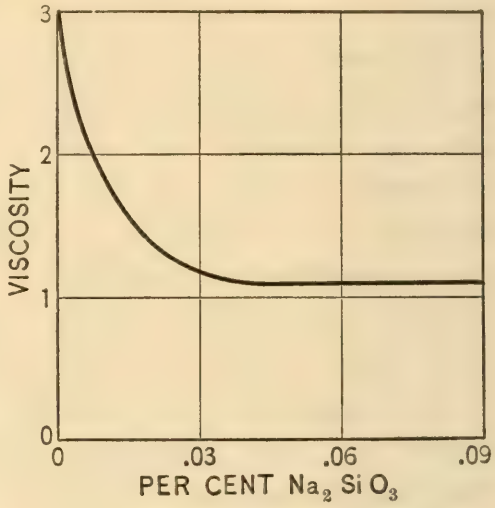

FIG. 9.—*Effect of sodium silicate on Tennessee ball clay body*

that the alkalies are being neutralized by the salts of the ball clay, but not yet sufficiently to cause flocculation.

4. FLORIDA KAOLIN BODY

This material in the form of a slip containing 50 per cent solids was found to offer considerable difficulty in regard to obtaining constant viscosity readings. Upon making check readings the viscosity values were found to drop off continually. With increasing alkali concentrations this change seemed to become somewhat less prominent. This point may be illustrated by giving the figures for several sets of determinations, Table 2.

TABLE 2

Viscosity with Increasing Amounts of Na_2CO_3

0.03 per cent	0.06 per cent	0.09 per cent	0.12 per cent	0.15 per cent
2.95	2.62	2.30	1.76	1.72
2.90	2.61	2.18	1.77	1.72
2.74	2.34	2.16	1.68	1.77
2.54	2.25	2.07	1.68	1.79
2.38	2.26	1.99	1.65	1.72
2.40	2.24	1.91	1.62	1.68
2.40	2.24	1.82	1.59	1.59
2.40	.....	1.78	1.63	1.60
.....	.....	1.79	1.61	1.61
.....	.....	1.79	1.61	1.62

Similar variations, though not so marked, were encountered with Georgia kaolin, but not with North Carolina kaolin and

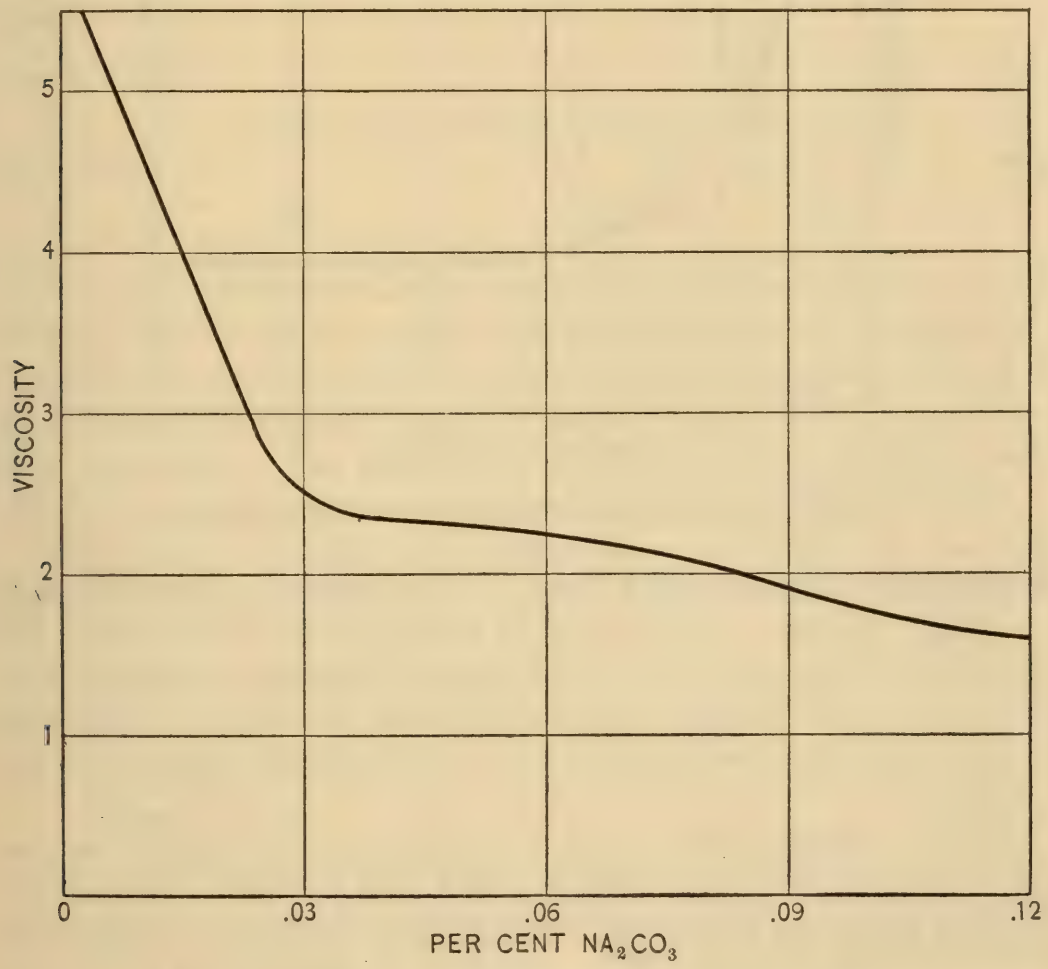

FIG. 10.—*Effect of sodium carbonate on Florida kaolin body*

Tennessee ball clay. Although the slips in each case were shaken, allowed to stand for as long as 72 hours after the alkali was added, and again shaken before the viscosity determination was made, the additional disturbance caused by pouring the slip evidently caused a further liquefying effect. Hence the preliminary drying to 110° C did not seem to prevent these changes.

Sodium Carbonate Series (*Fig. 10*).—It is observed from this

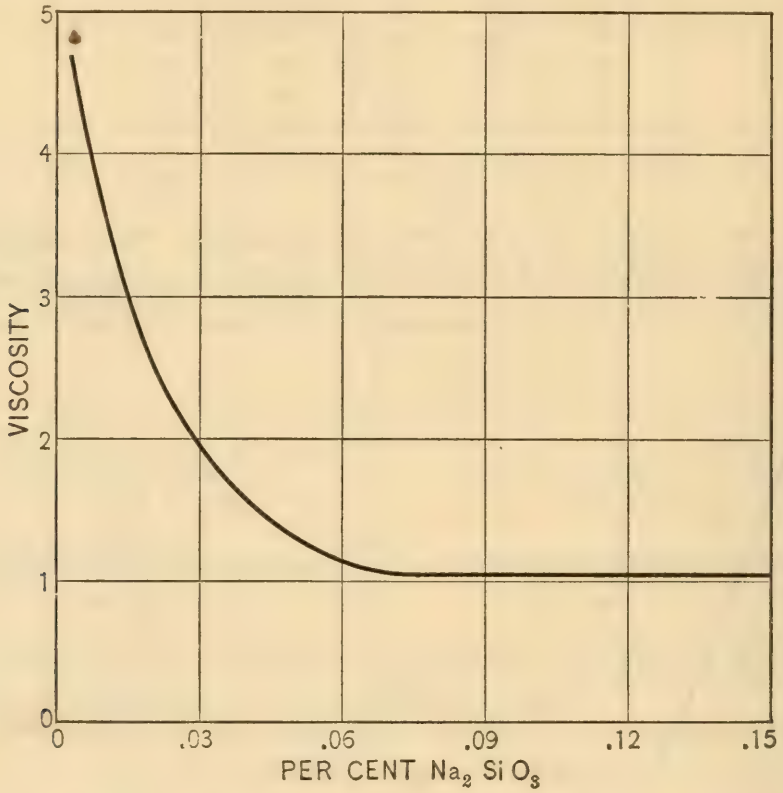

FIG. 11.—*Effect of sodium silicate on Florida kaolin body*

diagram that the viscosity drop is very decided. Starting with an initial viscosity so high that it could not be determined, the addition of 0.03 per cent of the reagent brought down the viscosity to 2.45. Further increments tend to lower the viscosity at a very much decreased rate, but a well-defined minimum is not reached.

Sodium Silicate Series (*Fig. 11*).—In this case again the viscosity drop is very great with 0.03 and 0.06 per cent of the alkali. Further additions appeared to bring about no more changes with

additions as high as 0.15 per cent. The sodium silicate proved to be more effective in its action than the carbonate.

In the course of this work it was observed that upon subjecting any of the slips to a vacuum large volumes of air were expelled even in completely deflocculated suspensions. It was thought desirable, therefore, to subject some of the slips to the vacuum treatment and to compare the viscosity with the previous value. These results are compiled in Table 3.

TABLE 3

Kind of body	Percentage addition of Na_2SiO_3	Viscosity before the vacuum treatment	Viscosity after the vacuum treatment
Georgia kaolin	0.03	2.60	2.94
Do	.06	2.32	2.72
Tennessee ball clay	.03	1.14	1.22
Do	.06	1.08	1.08
North Carolina kaolin	.03	1.43	1.50
Do	.06	1.34	1.39
Do	.12	1.33	1.40
Florida kaolin	.03	1.91	3.00
Do	.06	1.08	1.08

It would appear, thus, that a considerable amount of air is entrapped within the fine-grained clays, especially in the case of the more plastic ones. It seems also that this air appears to be held in a state of absorption, since no contraction in the volume of the slip was noted. The effect was more prominent with the lower alkali concentrations and with the Georgia and Florida kaolins.

In addition to these body mixtures another body, B, was prepared containing three of these clays in the following proportions:

	Per cent.
Feldspar	21
Flint	34
North Carolina kaolin	20
Florida kaolin	20
Tennessee ball clay	5

The initial slip in this case contained 55 per cent of solids. Only one series was run using sodium carbonate. The results are presented graphically in Fig. 12. The drop to minimum viscosity—from 3.5 to 1.25—with 0.06 per cent is quite marked, and

the rise toward another maximum is clearly indicated. The coagulating tendency is very gradual, and hence the deflocculation range is of generous extent.

A commercial casting body obtained through the courtesy of a Trenton firm was likewise studied. The composition of the body was not given. In this case a mixture of sodium carbonate and sodium silicate in equal parts was used. The results of this test are shown graphically in Fig. 13. It appears that this body, owing to its high ball clay content, requires for maximum deflocculation a content of 0.2 per cent of the reagent mixture. The

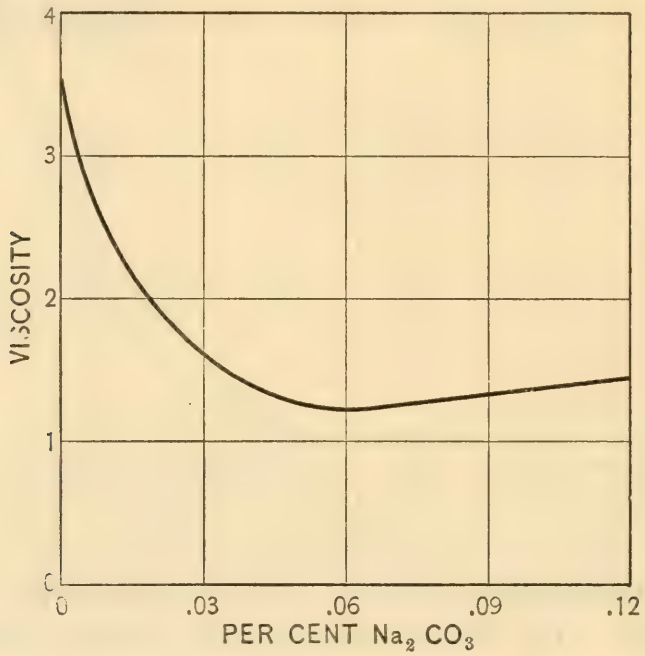

FIG. 12.—*Effect of sodium carbonate upon body B*

viscosity of the slip which contained 66.69 per cent solids, without any addition of alkali, could not be determined. The viscosity drop, corresponding to an alkali addition from 0.1 to 0.2 per cent, is quite marked—from 4.17 to 1.5. After maximum deflocculation is attained the condition of the slip appears to be quite constant and there is no evidence of any coagulating tendency. About 0.15 per cent of the reagents would appear to be the proper concentration for casting purposes, considering no other factors, such as after-stiffening.

VII. VISCOSITY OF CLAY MIXTURES WITHOUT ADDITION OF ALKALI

Our attention has been called to the fact that there is a certain interaction of mixtures of different clays as brought out by viscosity measurements. T. G. McDougal has informed us of interesting results obtained in this connection. In order to test out this point and to determine whether the addition of one clay slip to another caused regularly progressive or discontinuous changes

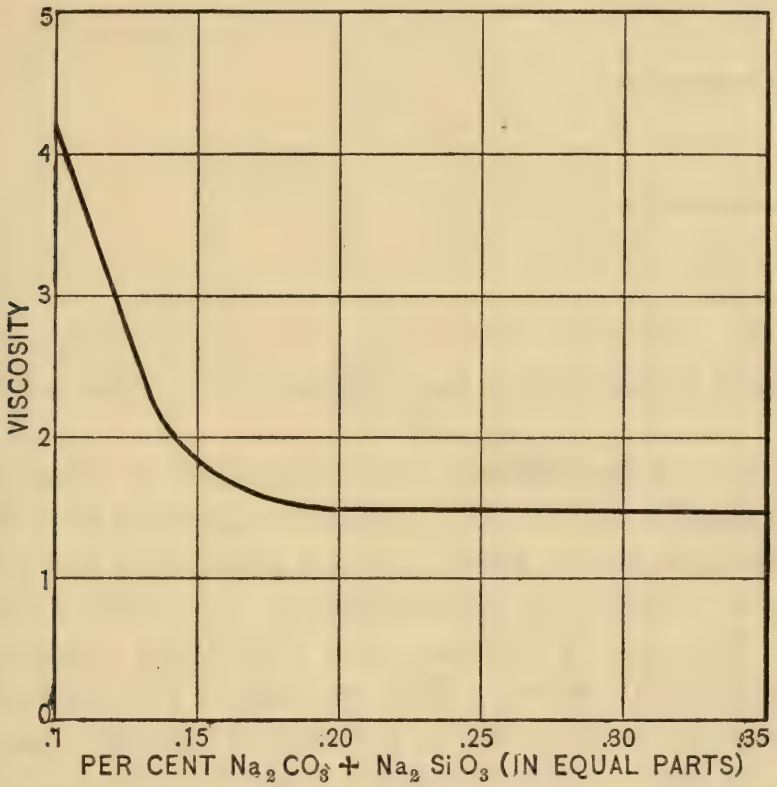

FIG. 13.—*Effect of sodium carbonate and sodium silicate mixture on Trenton casting body*

in viscosity, four porcelain body slips were prepared of North Carolina kaolin, Georgia kaolin, Tennessee ball clay, and Florida kaolin. The body composition was the same as that previously employed. The contents of solids in the above order were 53.8, 53.64, 53.67, and 42.27 per cent. The viscosities of these bodies were found to be 1.21, 1.08, 1.80, and 2.94. The mixtures were then made so that the North Carolina kaolin body slip was blended with each of the other three bodies in the proportion of 1:1, 2:1,

3:1, and 4:1, on the basis of dry weights. The contents of solids for the various blends were as follows:

TABLE 4

Mixture of bodies	Ratio of North Carolina kaolin to other body	Percentages of solids in slip
North Carolina-Georgia kaolins	1:1	53.52
Do	2:1	53.55
Do	3:1	53.78
Do	4:1	53.26
North Carolina-Tennessee ball	1:1	54.02
Do	2:1	53.60
Do	3:1	53.56
Do	4:1	53.26
North Carolina-Florida kaolin	1:1	51.36
Do	2:1	53.69
Do	3:1	53.82
Do	4:1	53.88

The bodies before having been made up into slips were dried at 110° C.

The results of the viscosity determinations of these series are shown graphically in Fig. 14. It will be observed that the North Carolina-Georgia kaolin series shows a practically linear relation, indicating no interfering phenomena in the mixture of the two systems. The case is different with the North Carolina kaolin-Tennessee ball clay series. Here, as long as the kaolin predominates, down to the ratio of 2:1, no marked change occurs. With an excess of ball clay in the ratio 1:1 sudden coagulation occurs, and the viscosity rises rapidly to a value considerably above that reached by either body slip alone. In the North Carolina-Florida kaolin series the viscosity rises with the increase in the more plastic constituents, but shows a decided drop when the ratio 1:1 is reached. The reason for this decrease is not evident. These results are sufficient to show that interaction between different clays occurs in slips, and these may have decided influence upon the behavior in the casting.

VIII. ABSORPTION OF ALKALIES BY CLAY

In order to determine the degree to which clays absorb alkaline salts, mixtures of Florida kaolin, Georgia kaolin, and Georgia kaolin with 50 per cent flint were treated with solutions of NaOH and Na_2CO_3 of different concentrations. The procedure consisted in weighing out samples of the materials, adding a constant volume of the solution, and rapidly filtering by suction in a vessel containing air previously passed through KOH. By titrating for

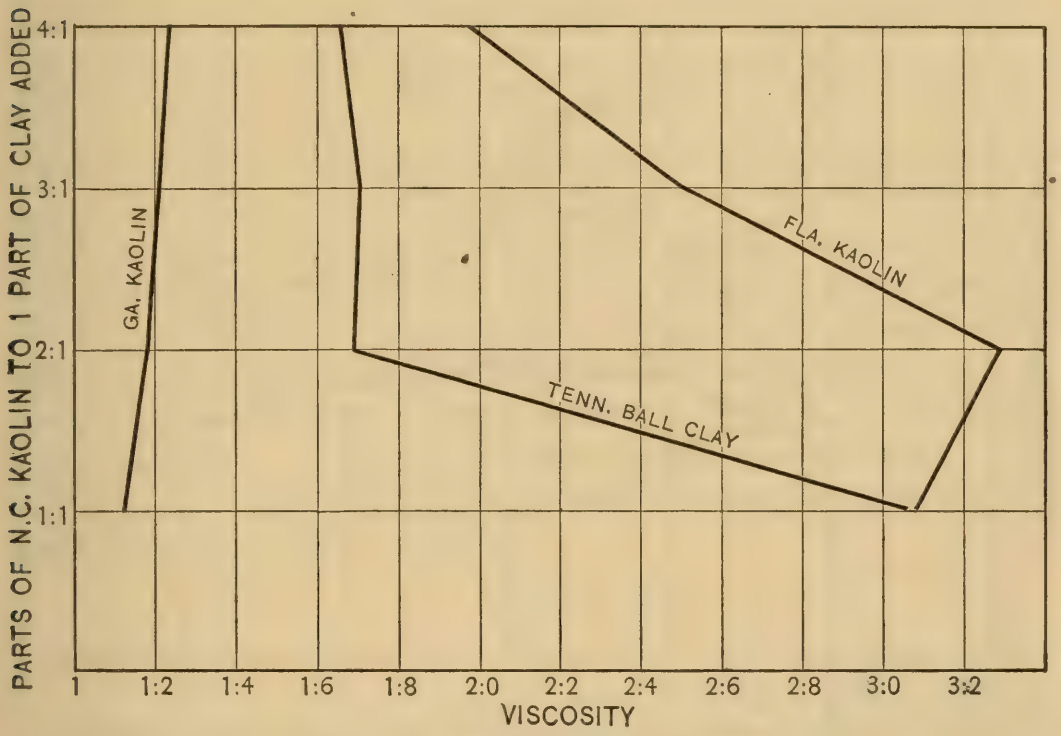

FIG. 14.—*Viscosity of clay mixtures*

the alkali content per cubic centimeter of the original solution and in the filtrate the amount absorbed was readily found. The results of this work are shown in Fig. 15. In this diagram the alkali content is expressed in terms of percentage of the dry clay. The maximum absorption of Na_2CO_3 in Florida kaolin is 0.16 per cent of alkali added, being 40 per cent of 0.4. The amount absorbed from the more dilute solutions increases with the concentration and appears to remain constant at the above value.

The same clay mixture absorbed a far greater amount of NaOH, namely, 0.28 per cent, or 56 per cent of 0.5. Since the absorp-

tion with both 0.4 and 0.5 per cent is practically the same, it appears as if the amount absorbed approached constancy, though it is but reasonable to suppose that some reaction with the silica of the clay should occur, especially with higher concentrations of NaOH.

With the Georgia kaolin-flint mixture the absorption with 0.4 and 0.5 per cent Na_2CO_3 added is practically the same, being 0.23

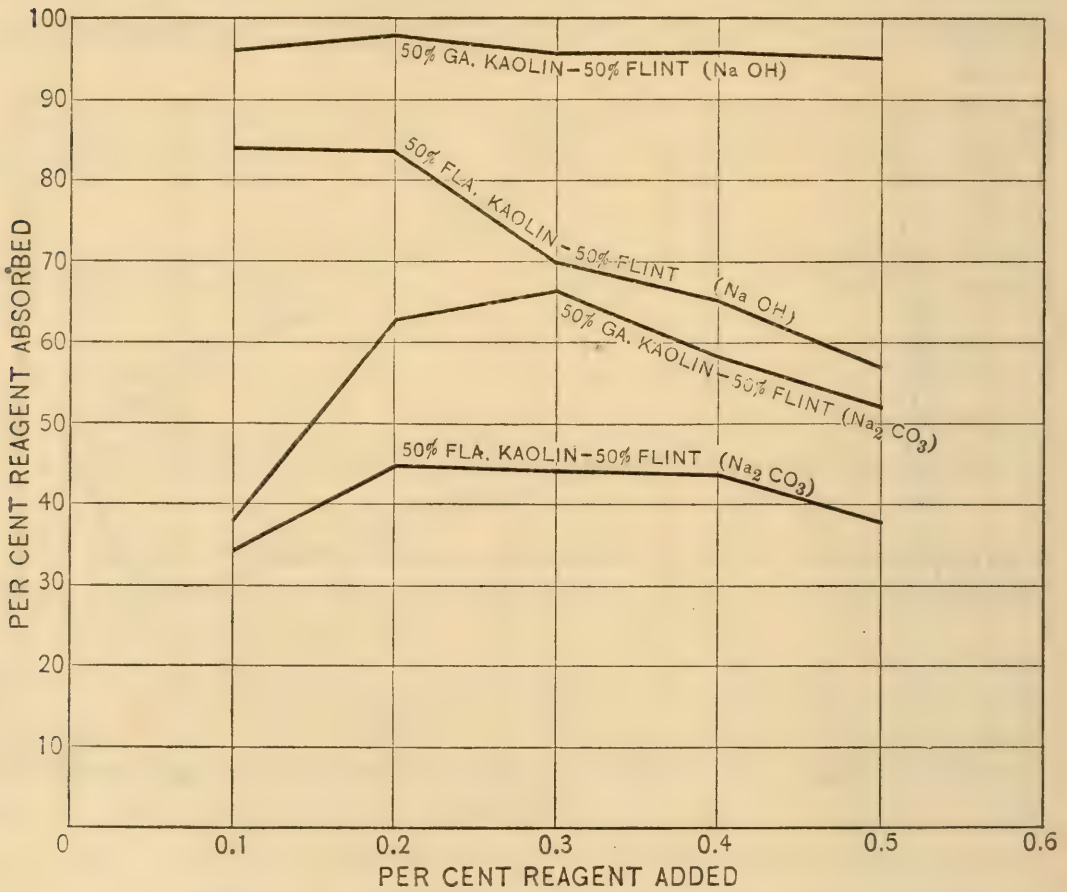

FIG. 15.—*Absorption of alkali by clay-flint mixtures*

and 0.26 per cent, respectively. These values, therefore, appear to be practically constant for this clay.

The Georgia kaolin-flint mixture appeared to absorb about 95 per cent of the NaOH added for practically all concentrations. This indicates chemical reaction with the clay, and we are evidently not dealing here with a case of simple absorption.

From these data it seems, therefore, that absorption of the alkalies plays an important rôle in casting slips. The greater absorption of NaOH is probably responsible for the greater

effectiveness of sodium silicate in the liquefaction brought about. Whether or not the content of the Na_2CO_3 absorbed is a criterion of the degree of dispersion of clays remains to be demonstrated, but the indications are that it might do so.

IX. TENSILE STRENGTH TESTS OF BODY MIXTURES

In order to throw light upon the effect of the alkaline reagents in regard to the structure of cast bodies, the tensile strength of briquettes dried at 110° C and formed by casting in suitable plaster molds was determined. The same single clay bodies studied before were used for this work and five series of 10 briquettes were made from each body. These were (*a*) briquettes cast from the slip without addition of reagent; (*b*) briquettes cast from the slip with addition of Na_2CO_3 corresponding to the point of maximum deflocculation (minimum viscosity); (*c*) test pieces cast from slip with a concentration of Na_2CO_3 equivalent to a point to the left of minimum viscosity; (*d*) briquettes from slip with an addition of Na_2SiO_3 necessary to produce maximum deflocculation; (*e*) specimens from slip containing an amount of Na_2SiO_3 corresponding to a point to the left of minimum viscosity.

The same tests were made also with the casting body B. The results are compiled in Table 5.

TABLE 5

Body containing as clay	Without reagents (lbs. per sq. in.)	Na_2CO_3. Maximum deflocculation (lbs. per sq. in.)	Na_2CO_3. Less than maximum deflocculation (lbs. per sq. in.)	Na_2SiO_3. Maximum deflocculation (lbs. per sq. in.)	Na_2SiO_3. Less than maximum deflocculation (lbs. per sq. in.)
North Carolina kaolin	14.9	17.8	14.0	14.7	17.2
Georgia kaolin	68.0	87.1	78.6	100.7	89.7
Tennessee ball clay	102.5	153.8	136.3	168.3	131.3
Florida kaolin	65.7	70.5	62.4	56.5	62.5
Body B	.....	67.33	73.2	59.0	91.1

From these results it appears first that the strength of cast bodies containing the alkaline reagents is greater than that of the bodies cast without any additions. Second, in bodies containing but a single clay, the state of maximum deflocculation does not,

as might be expected, result in weaker structure than when the bodies are carried to a point to the left of minimum viscosity; in fact, the opposite is the case. It is possible, of course, that owing to the small volume of the briquettes the calcium sulphate taken up from the molds might have exercised some influence.

X. THE CONSTANT OF THE GENERAL VISCOSITY FORMULA

Owing to the fact that the general formula makes the assumption that the viscosity of a dispersed system composed of spherical particles is a linear function of the volume of disperse phase, which we know from previous investigations is not true for clays in high concentrations, it was thought desirable to determine the constant of the expression for several concentrations of clay slips. For this purpose the exceedingly fine-grained washed Florida kaolin was used. Three concentrations were prepared containing, respectively, 10.58, 18.96, and 21.23 per cent of solids. The viscosities as measured by the efflux tube were 1.043, 1.55, and 2.83. Calculating the volume of the dispersed matter by dividing by the specific gravity of the clay, 2.6, and the volume of the system, we obtain for

Case I

$$1.043 = (1 + \frac{4.07}{93.49} k);$$

solving for k we have the value $k = 1$.

Case II

$$1.55 = (1 + \frac{7.29}{88.3} k);$$

solving, $k = 6.25$.

Case III

$$2.83 = (1 + \frac{8.15}{86.92} k);$$

solving, $k = 19.4$.

The value of k therefore increases rapidly with the content of solid and in using this relation for the calculation of the viscosity for any given concentration, or vice versa, it will be necessary to compute this value for a series of concentrations so as to obtain a curve

expressing this relation. In case such a calculation is applied to a casting slip the percentage content of alkali in terms of the dry weight of the materials must be kept constant or else discrepancies will appear.

XI. THE TIME FACTOR

The change in the viscosity of slips with time is a very important factor in casting practice. Considerable trouble ensues frequently owing to the use of variously aged slip. Thus in one case a slip proved to work very satisfactorily after 24 hours blunging, but

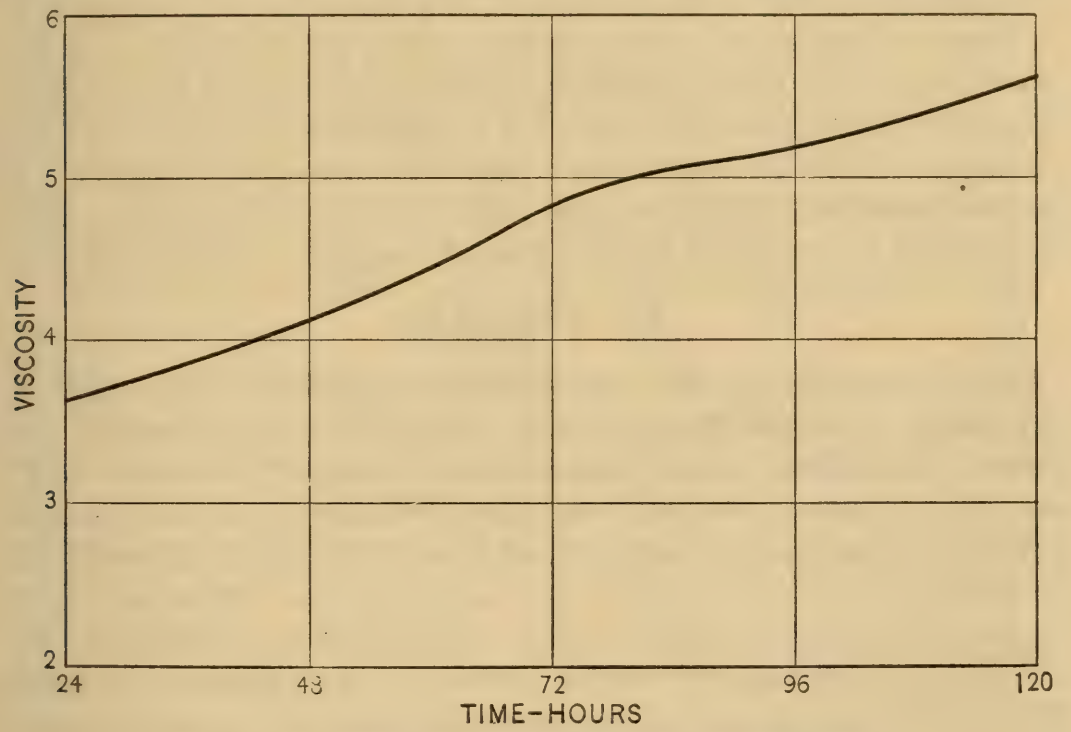

FIG. 16.—*Change in the viscosity of a body slip with time*

showed a decided "livery" consistency, due to coagulation, after three days. This phenomenon was constantly met with in the present work and was not overcome by the predrying of the clay body at 110° C. It seemed to be evident also that the slips containing alkali just sufficient to bring about maximum deflocculation, or less than this amount, were more apt to show fluctuation in viscosity than those containing more than the required amount. The time factor is explained, first, by the fact that the action of the alkalies upon the dispersed matter is often quite slow unless vigorous agitation is kept up constantly. Second, the concentration of

alkali may change also because of absorption and reaction with silica or the soluble sulphates. The latter salts play an especially important part in the case of ball clays, which, as is well known, may diminish the liquefying action of the alkalies in a very decided manner or require the addition of an excess of the alkali. According to the nature of the clays and the content of the reagents the time effect may consist in further deflocculation or in coagulation of the slip. Clay slips containing no alkaline reagents are subject to even greater variations in viscosity than casting slips. The accompanying diagram (Fig. 16) shows the gradual coagulation of a practical casting body containing 0.1 per cent of a mixture of sodium carbonate and sodium silicate. This phenomenon does not take place with higher concentrations of alkali. It is necessary therefore in preparing casting slips to know the time effect so as to counteract it by properly regulating the content of reagents. It is quite possible that the organic colloids of the ball clay may tend to exercise a protective influence on the stability of the system.

XII. SUMMARY

It has been shown that the washing of kaolinitic clays may be decidedly improved as far as the quality of the product is concerned by adding to the water in the blunger a definite small amount of caustic soda or a mixture of caustic soda and sodium silicate. This makes possible more complete sedimentation of the granular impurities which it is desired to remove. This treatment improves the color of most clays, enriches their content in clay substance, decreases the drying shrinkage, but tends to increase the burning shrinkage. Clays containing iron in the form of finely divided ferric oxide can not be treated successfully by this process.

The electrical osmosis process plays no important part in the purification of clays. Its function is that of mechanically depositing particles in suspension upon the positive electrode. It thus replaces the filter press, and if the latter is of a modern improved type any advantage resulting from continuous and automatic operation will be more or less neutralized. The higher the voltage of the current employed the denser will be the deposit of clay and the lower the water content. The preliminary sedimentation process, using caustic soda or other electrolytes, seems to be the real feature of the osmose process. The electrical method of separa-

tion can not remove finely divided ferric oxide. It also deposits with the clay any finely divided quartz which may be in suspension.

The efflux viscosimeter appears to be satisfactory for the technical study of casting slips. The kinetic and temperature corrections applied in precise measurements are not necessary for the purpose in view.

Sodium silicate is a more effective reagent as far as the reduction of viscosity is concerned than sodium carbonate.

North Carolina kaolin in suspension is not influenced by the reagents in question in a marked manner, because of its comparative coarseness.

Georgia kaolin has a far greater initial viscosity than the North Carolina kaolin and appears to be very sensitive to additions of sodium carbonate. It shows a well-defined minimum of short range, which turns toward a maximum. Its range at minimum viscosity is greater when sodium silicate is used.

Tennessee ball clay No. 3 gives no indication of a decided minimum viscosity point.

Florida kaolin responds decidedly to the addition of sodium carbonate, but a well-defined minimum is not reached, probably due to the comparatively large amount of pseudoemulsoid or lyophile substance produced. With sodium silicate the viscosity decrease is equally great, with no tendency to approach another maximum value.

A large volume of air seems to be absorbed in clay slips, the removal of which increases the viscosity. Thorough and vigorous stirring of the slip therefore seems essential, and exhaustion by vacuum might be beneficial. The effect of the entrapped air was more prominent with lower alkali concentrations and with the Georgia and Florida kaolins.

A body containing North Carolina kaolin, Florida kaolin, and Tennessee ball clay responded well to the addition of sodium carbonate, but showed a turn toward greater viscosity (recoagulation) for additions greater than 0.06 per cent.

A commercial slip fairly high in English ball clay showed a rapid drop in viscosity, but required a much higher percentage of the reagent mixture than the single clay bodies. The viscosity seemed to remain constant at the minimum value. It is possible that

this condition is due to the presence of organic colloids which exercise a protective influence.

Interaction occurs between different clays with respect to viscosity changes independent of the alkali additions, and these are not necessarily proportional to the ratios of the admixed clays or regular in character. It is important therefore to know just what this interaction is, since it is quite possible that some clays may have a detrimental effect upon the others in making up the casting body. The ball clay content in a casting slip should be reduced to the minimum.

Absorption of the alkaline reagents plays an important rôle in casting slips. Sodium hydroxide is absorbed to a far greater extent than the carbonate and probably combines chemically with the clay.

The tensile strength of cast bodies containing alkali additions may be greater than that of the same materials cast without these reagents. Single clay body slips used in the state of maximum deflocculation do not seem to be weaker than when the suspensions are only carried to a point to the left of minimum viscosity.

The general formula, $n_1 = n\ (1 + kf)$, where f = ratio of volume of dispersed particles to total volume of system and in which k is determined for each of a series of concentrations, might prove useful for interpolation purposes, provided the alkali addition is kept constant.

Casting bodies with low concentrations of alkali are more apt to change their viscosity with time than those containing larger additions.

The writer wishes to express his indebtedness for assistance in this work to Messrs. G. H. Brown, M. R. Hornung, C. S. Kinnison, and W. L. Howat.

WASHINGTON, May 27, 1915.

DEPARTMENT OF COMMERCE

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ELECTROLYSIS AND ITS MITIGATION

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I. INTRODUCTION

In the effort to reduce or eliminate damage to pipe systems and other subsurface metallic structures due to stray earth currents from street railways, a great many methods have been proposed or tried. Some of these have been widely used with more or less benefit in many instances and apparent failure in others. The Bureau of Standards has been engaged for some time past in a general investigation of the subject of electrolysis and its mitigation, the work being carried on by special appropriations granted by Congress for the purpose.

This investigation has included a study of the physical laws governing electrolytic and self-corrosion in soils, an extended investigation of the effects of electric currents on plain and reinforced concrete, and a study of the work of previous investigators relating to the subject of electrolysis and its prevention. Many laboratory investigations have been carried out, and also experiments on artificial pipe lines laid especially for the purpose of permitting experiments under actual conditions with various methods of electrolysis prevention. This work has been supplemented by a large amount of field work in various cities with a view of obtaining first-hand information in regard to the effectiveness of different methods of mitigation as they are commonly applied and to develop methods of making electrolysis surveys and giving any special information desired. The results of these investigations are being published in a number of special reports, a list of which is given at the end of this paper.

The present report is confined principally to a discussion of the subject of the prevention of electrolysis in metallic structures, including gas and water systems and lead-covered cables. The discussion and conclusions presented here are based on the studies above referred to in so far as they yield definite results to the present time. The work is still incomplete, however, and much remains to be done in the investigation of special problems relating to some of the more important methods of electrolysis mitigation. As the work progresses supplementary reports will be made from time to time as the results of the investigation seem to justify.

Although many of the methods of mitigation hereinafter discussed are of limited application, and some of them either worth-

less or positively injurious, still, in view of the fact that they have been seriously proposed from time to time by engineers of standing, it has been deemed advisable to discuss rather fully the field of usefulness of each particular method, setting forth the reasons for its limitations or dangers, as the case may be. A few of the most important methods, however, have been discussed in detail and a considerable amount of experimental data obtained by the engineers of the Bureau of Standards has been presented as a basis for the more important conclusions and recommendations that are presented in this report.

II. GENERAL CONSIDERATIONS REGARDING ELECTROLYSIS

1. COMPARISON OF THE ELECTROLYSIS PROBLEM IN AMERICA WITH THAT IN OTHER COUNTRIES

Almost immediately following the introduction of electric railways serious trouble from electrolysis of neighboring underground pipes was experienced. This rapid development of acute electrolysis trouble was due mainly to the fact that during the earlier stages of electric railway development relatively little care was taken to maintain good bonding of the rail joints, and as a result of the neglect of this feature it very frequently happened that practically all of the railway return current was compelled to return to the region near the power house by way of the earth, much of it finding its way to the pipes and causing serious corrosion where it flowed again from the pipes into the earth near the power house.

In Great Britain the advent of the trouble was very soon followed by the adoption of somewhat stringent regulations for reducing the damage. These took the form of regulations limiting the voltage drops in the negative return, the most important of which was a rule limiting the voltage drop between any two points in the negative return to 7 volts. The immediate result of this limitation of voltage drop was to bring about better bonding of the track return and the installation of negative return feeders for returning current to the power houses. This was followed by almost complete mitigation of electrolysis troubles, and since that time the electrolysis problem in Great Britain has not been a serious one. More recently the problem has been attacked

from a similar standpoint in many cities of continental Europe, and regulations in some respects more stringent than those in effect in Great Britain have been put into effect. As a result very good electrolysis conditions generally prevail in Europe, and in rare instances only has the trouble developed to an acute stage, such as is commonly experienced in this country.

In America, on the other hand, a very different course was pursued. No progress was made toward imposing voltage regulations for the negative return, and although in time more and more attention was paid to track bonding, which retarded the trouble somewhat, the principal reliance from trouble was placed on other methods, one of the most generally used being that known as "pipe drainage." This method of mitigation consists essentially in connecting the underground metallic structures to be protected directly to the rails or railway negative bus by means of copper cables, in all places where the underground pipes or cables tend to become positive to the railway return circuit. This method has been almost universally used by telephone and power companies for the protection of lead cable sheaths, and it has been used to a considerable extent in connection with underground pipes. More recently insulating joints have been used in many installations and this usage is rapidly becoming common practice, particularly with many gas companies, and not a few water companies have used insulating joints with considerable success.

Pipe drainage, however, is a treatment essentially symptomatic in character, this measure being designed to minimize the immediate destructive effects of the stray currents without tending in any way to remove the cause of such stray currents. Notwithstanding the application of these various measures to the pipes, the trouble from electrolysis is becoming increasingly important in this country because of the rapid development of electric railway lines and the increase in traffic, and it is probable that more trouble from this source is now being experienced in this country than anywhere else in the world. Recently, however, this subject has been given more serious attention by the railway companies as well as the owners of underground utilities, and at the present time various national engineering organizations have taken up

the matter in a systematic way, and there is reason to believe that substantial progress toward the eradication of this evil will be made in the near future.

2. ELECTROLYTIC CORROSION PROPER

Electrolytic corrosion of underground structures occurs in general wherever current flows from the metallic structure into the earth. The most common cause of these stray currents in practice is primarily the drop of potential in the railway return circuit (proportional to its resistance and to the current flowing in it), as a result of which those portions of the track more remote from the power house will be at a potential above the earth, whereas those portions of the track near the power house will in general be at a potential below that of the earth. In consequence of this, current tends to flow from the tracks to the earth in the more outlying districts and from the earth to the tracks in the region near the power house. These currents after getting into the earth tend to flow as a rule in the general direction of the power house, and they gradually accumulate on any underground pipes and cables that run in the same general direction, but when they reach the region near the power house in which the earth and the pipes embedded therein are at a higher potential than the railway tracks, these currents are again discharged through the earth to the negative railway structure, and it is in this region that the damage to the pipes most frequently occurs.

This region in which the currents are flowing from the pipes into the earth is called the positive area and the outlying region where the currents are flowing from the earth into the pipes is called the negative area. This definition of positive and negative areas is very general, however, and it is not safe to assume that trouble is confined to the so-called positive area. Many places will be found where, owing to high resistance in the joints, the currents will be forced to leak off the pipes and flow through the earth around the joints, thus making a small positive area on one side of the joint and a small negative area on the other side of the joint. Such local positive areas may be found in what is generally known as the negative region, and where these occur corrosion of the pipes may take place although the pipe systems in general are found to be negative to the railway tracks.

Further, two pipe systems occupying the same territory may both be decidedly negative to the railway return, but one more strongly negative than the other. In this case the two pipe systems will be at different potentials and one will discharge current into the other and thus give rise to corrosion on the pipe system at the higher potential, although readings might show that it is at all points negative to the railway return. In determining whether or not a pipe or cable is undergoing electrolytic corrosion it is necessary to determine not only whether it is positive to the railway system but also whether it is positive to any surrounding structure.

When current is discharged from a pipe or cable sheath into the earth the amount of corrosion which take place is roughly proportional to the product of the current strength into the time during which the current flows; in other words, to the quantity of electricity that has been discharged by the pipes. If the structure be iron pipe, the amount of corrosion under most conditions in wet soils will be about 20 pounds per ampere per year, and in the case of lead cables the corrosion will be approximately 75 pounds per ampere per year. In many cases, however, both with iron and lead, either more or less than this theoretical amount of corrosion will take place. This is especially true in relatively dry soils where the corrosion is generally very much less than the figure here given. Extensive investigations have shown, however, that the actual corrosion that takes place in the case of iron varies in different cases from 10 to 25 pounds per ampere per year.

It is not possible, however, to determine the amount of damage to the pipe structure by determining the amount of current which it is discharging from any given portion of its length and calculating therefrom the amount of corrosion which takes place. The reason for this is not alone the uncertainty in the total amount of corrosion just referred to, but more particularly it is due to the fact that the corrosion is in practically all cases very unequally distributed over the surface of the iron, there being a marked tendency for the current to be discharged locally, producing the phenomenon commonly known as pitting. In this manner a small hole may be eaten entirely through the pipe thereby destroying its usefulness, while the average corrosion over the surface of

the pipe may be relatively small. Figure 1 shows an example of a pipe that has been corroded by stray currents, and which exhibits the characteristic pitting that has been almost universally encountered.

3. SELF-CORROSION

Self-corrosion is very generally regarded as being due primarily to the presence of local galvanic currents at the surface of the corroded metal, due either to physical differences between adjacent points on the surface of the metal or to foreign conducting substances in the soil. For example, if a piece of carbon in the form of coke be embedded in the soil in contact with the pipe surface at one point there will be a difference of potential between the coke and the pipe and a current will flow from the pipe through the moist soil to the coke and return to the pipe through the contact point between the two. The action here is exactly analagous to the action in a primary battery in which a piece of zinc and a piece of carbon are immersed in the electrolyte and connected together through an external circuit. A current flows through the electrolyte from the zinc to the carbon, thereby corroding the zinc. The electromotive force given by iron or steel when embedded in ordinary soils in contact with coke is usually about 0.6 volt, and this is sufficient to give rise to very rapid corrosion and pitting of the iron surface. Action of this kind is frequently encountered where pipes are embedded in soils containing cinders in which particles of coke may be found.

Galvanic action of this kind also takes place as a secondary action following electrolysis from stray currents. If stray currents are discharged from a pipe producing initial corrosion, the corroded iron thus carried into solution in the soils comes in contact with oxygen dissolved in soil water which results in the precipitation of iron oxide on the surface of the pipe. This iron oxide is a conductor of electricity, and it also exhibits an electromotive force against iron, as in the case of the piece of coke. Hence, where iron oxide is thus deposited on the surface of the iron at any point, corrosion may continue to some extent even though the stray currents which initiated the trouble have been removed. Self-corrosion may also occur from galvanic action due to physical differences between different points of the surface

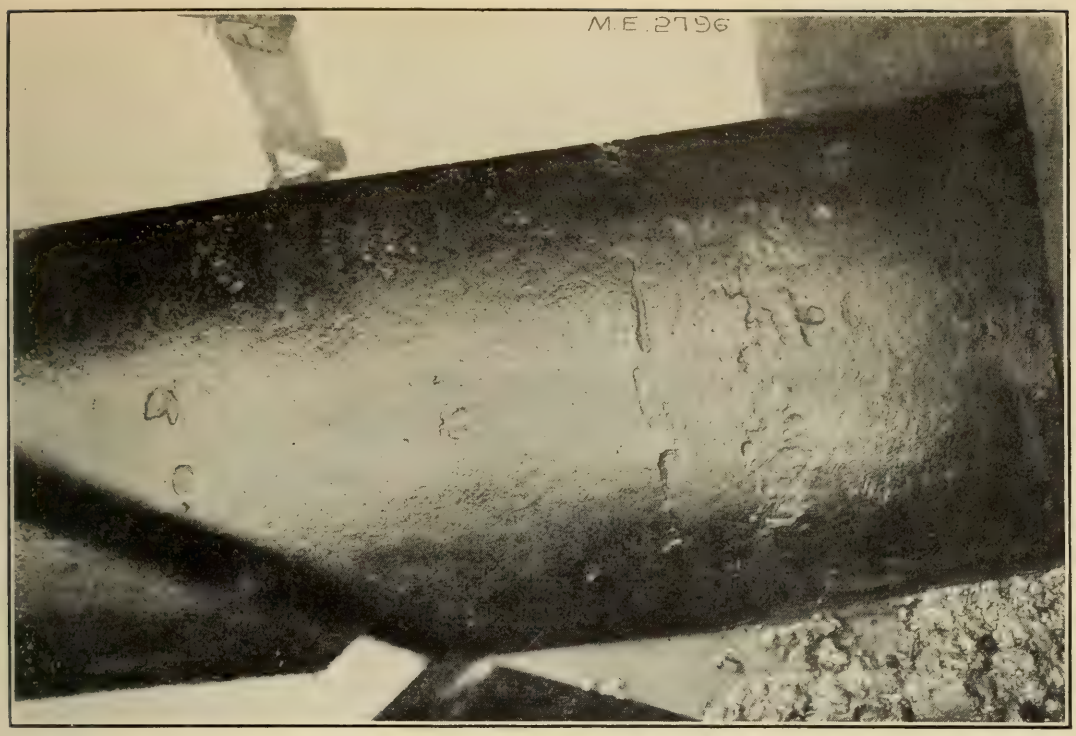


FIG. 1.—*Example of electrolytic corrosion*

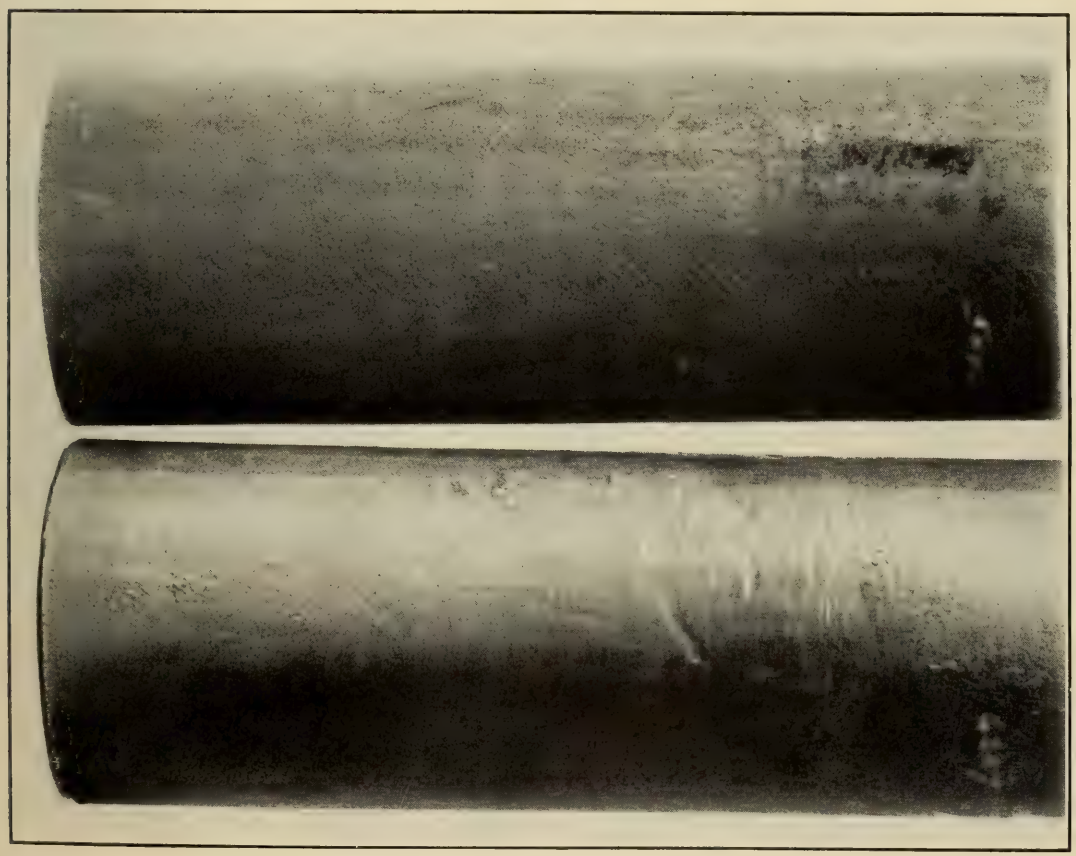


FIG. 2.—*Example of self corrosion*

of the iron itself, or due to differences in the electrolyte in the soil near to adjacent portions of the iron surface.

Unfortunately, self-corrosion generally manifests itself in a manner very similar to that caused by stray currents. This is shown quite clearly in Fig. 2, which is a photograph of two pieces of cast-iron pipe corroded under conditions such that no stray currents could exist. It will be seen that the pipe exhibits pitting very similar to that caused by electrolytic corrosion. Because of this similarity in appearance it is not possible in general to determine by inspection of a corroded pipe whether or not the corrosion was caused by stray currents or by local galvanic action. Owing to this fact it not infrequently happens that cases of pipe corrosion are charged to the railway companies when the damage was actually due to local causes arising from the nature of the soil or of the pipe, or both.

The only sure way of determining whether or not stray currents are causing corrosion in any particular case is by making proper electrical tests to determine whether or not the pipes are actually discharging current into the earth. In a case where serious corrosion has been caused by stray currents and the cause of these stray currents later removed, the only certain way of determining whether or not the previous corrosion was caused by stray currents or by local influences is by making actual corrosion tests in the soil under the same average conditions of moisture and using the same kind of iron as was previously found corroded. In the absence of a test of this kind it is not possible to fix with certainty the cause of the damage.

4. TROUBLES FROM STRAY CURRENTS OTHER THAN CORROSION

While it is no doubt true that by far the greater portion of damage caused by stray currents takes the form of corrosion of underground pipes and cables there are certain other dangers resulting from these stray currents that deserve consideration. Among these may be mentioned overheating of pipes in buildings due to the flow of excessively heavy currents therein. Cases of this kind have been brought to our attention in which service pipes and their connections have been heated to a red heat by stray railway currents flowing through them, and where lead service

pipes have been melted off. Such extreme cases are of course rare, but when they do occur the fire hazard accompanying them may at times be serious. Another danger from the presence of stray currents on pipes is that due to the possibility of explosion of gases. Wherever any considerable amount of stray current is found on a gas pipe it is necessary to bond around any contemplated break in the continuity of the pipe, otherwise the arc which would occur between the pipe sections when disconnected would be likely to ignite escaping gas with possibly serious consequences. These various dangers will be referred to again later.

5. ELECTROLYSIS IN CONCRETE AND IN STEEL BUILDINGS [1]

(*a*) *Anode effects.*—During the last few years it has been observed that when an electric current flows through reinforced concrete certain effects are produced which may result in the destruction of the concrete structure. The first of these to be observed is known as the anode effect, first described by A. A. Knudson,[2] which occurs under certain circumstances when current passes from the reinforcing material out into the concrete. The action here is essentially the same as when current is discharged from a pipe into the earth, namely, the surface of the iron is corroded; but the effects of this case are even more serious than in the corrosion of pipes because of the secondary actions which take place.

As soon as iron is carried into solution by the electric current it comes in contact with oxygen in the concrete and there is formed a precipitate of iron oxide. This occupies a volume of about 2.2 times the volume of the original iron, and there results a swelling action which in time may become sufficient to split even very large masses of concrete. The character of the results of this action are shown in Fig. 3, which shows a block of concrete with an embedded iron electrode which has been exposed for some time to the flow of current from the iron into the concrete.

It is very important from the practical standpoint to bear in mind, however, that the disastrous results shown in Fig. 3 occur only under special conditions which are not likely to be frequently

[1] For a full discussion of the subject of electrolysis in reinforced concrete, see Technologic Paper No. 18 of the Bureau of Standards.

[2] Electrolytic Corrosion of Iron and Steel in Concrete, trans. A. I. E. E., Vol. 26, p. 231, 1907.

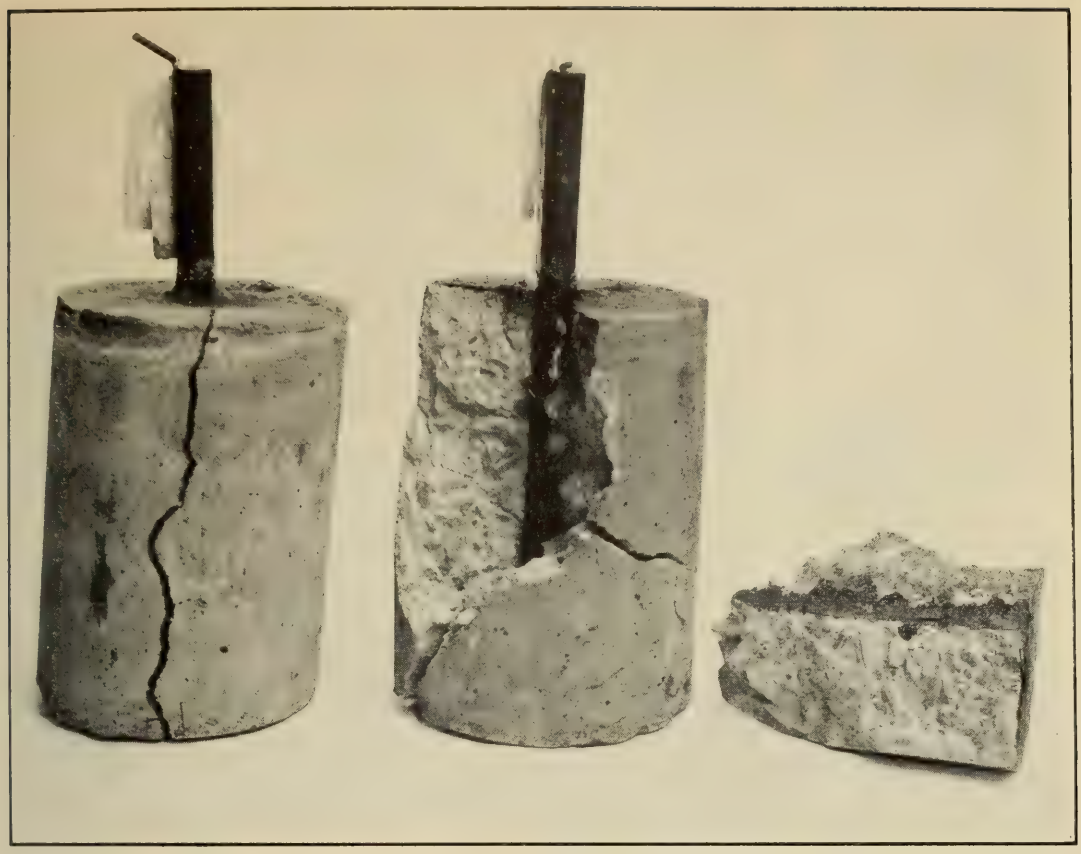


FIG. 3.—*Anode effect in concrete*

FIG. 4.—*Cathode effect in concrete*

encountered in actual practice. Extensive investigations have shown that in the case of ordinary concrete this rapid corrosion of the embedded iron with the resultant cracking of the concrete takes place only when the potential gradient impressed on the specimen is quite high—much higher, in fact, than would generally be encountered from stray railway currents. If the voltage on specimens of ordinary size such as might be used in buildings is kept as low as 2 or 3 volts or less, long time experiments have shown that practically no damage to the concrete results. It is therefore only under very extreme conditions that serious trouble of this kind is likely to be met in practice. However, it may occur; as for example, when an electric light wire becomes grounded on a metallic conduit embedded in concrete. The voltage here would generally be high enough to cause corrosion of the conduit and any reinforcing material that might be electrically connected therewith, which would result in ultimate splitting and more or less complete local destruction of the concrete structure; this is therefore a danger which under certain conditions should be guarded against. For this reason it may be well not to embed metal conduit in concrete structures where the character of the building is such that this is not necessary, nor should the conduit be electrically connected to the reinforcing material.

It is important to call attention to the fact that while, as above stated, in ordinary normal concrete with only 2 or 3 volts or less acting on concrete structures of the sizes usually encountered in practice, serious corrosion or cracking of the concrete will not occur, such corrosion and cracking will develop if any appreciable amount of salt is added to the concrete either during or after construction. It has been conclusively shown by years of experience that ordinary concrete affords a good protection for iron against natural corrosion, and recent investigations have shown that under ordinary circumstances it also affords a fair degree of protection against electrolytic corrosion. The addition of a small quantity of salt, however, has been found to destroy completely the protective effect against electrolytic corrosion. For this reason it is very important that no salt be used in the erection of reinforced concrete structures wherever there is any likelihood of stray currents from any source getting into the reinforcing material.

(*b*) *Cathode Effect.*—Another effect of electric currents on reinforced concrete has only recently been discovered. This is the cathode effect, and it occurs only where the current flows from the concrete toward the reinforcing material. In this case there is no corrosion of the iron at all, but there is a gradual softening of the concrete at the surface of the reinforcing material, due to the gradual concentration of alkali at the cathode. This softening begins at the surface of the iron and very slowly progresses outward into the concrete, often requiring many weeks or months to progress a distance of a sixteenth of an inch. The practical importance of this phenomenon lies in the fact that the softening of the concrete at the surface of the reinforcing material, although usually confined to a thin layer, is nevertheless sufficient practically to destroy the bond between the iron and the concrete, and in this way a structure may be weakened or destroyed.

The cathode effect has been found to occur not only on high voltages, as in the case of the anode effect above described, but also on relatively low voltages, the rate at which it progresses being roughly proportional to the voltage applied in any particular case. Examples of trouble of this kind are shown in Fig. 4, which shows very definite regions of softened concrete surrounding the embedded iron. Because of the fact that this softening of the concrete near the cathode progresses at a much lower voltage than is generally required to produce the anode effect previously described, this cathode effect is likely to prove of greater practical importance than the cracking of the concrete at the anode which had previously been observed.

In regard to the actual dangers to which reinforced concrete structures in practice are subjected as the result of these phenomena, it should be emphasized that while cases of actual damage of this sort have been encountered in practice in a few instances, they are comparatively rare, and only in exceptional cases have conditions been such as to produce any appreciable amount of damage in actual building structures. We have had occasion to investigate numerous cases in which reinforced buildings or bridges have been damaged in which the damage was attributed to stray currents, but in most cases it has been found that the trouble was not in any way due to the presence of electric currents. In fact only

one case has up to the present time come to our attention in which any serious damage to a reinforced concrete structure has occurred in actual practice, except in those instances where salt was present in the concrete in considerable quantity. This emphasizes the importance of omitting salt in the construction of reinforced concrete buildings wherever there is any likelihood of stray currents getting into the structure.

III. METHODS OF MITIGATION APPLICABLE TO PIPES

The various methods of electrolysis mitigation that have been proposed are here treated broadly under two heads—first, those that may be applied to the pipe systems for protection of the pipes without regard to the extent of stray current leaking from the rails; second, those which are applied directly to the negative return of the street railway system and have for their object the prevention of leakage of electric current into the earth or the reduction of such leakage to so low a value that it will do practically no harm.

1. SURFACE INSULATION OF PIPES

Painting or otherwise insulating the surface of pipes, as by the use of treated papers and textiles, was early resorted to as a possible means of protecting the pipes from electrolysis, and this method is still used in some instances. It is doubtful, however, whether there exist any instances in which it has been definitely proven that insulating paints have effectively protected pipes from electrolysis for any considerable period of time, while there are many instances where they have failed utterly and where their presence has actually done harm. This statement may seem somewhat surprising to some who are familiar with instances where paints have withstood the action of soils for a long period and when uncovered both paint and pipe appeared to be in practically as good condition as when they were laid down. Practically all paints are classified as insulators, and it is quite natural that the impression should be more or less prevalent that these paints ought to prove effective as a protection against self-corrosion in the soil. In practice, however, such paints behave in a very uncertain manner at best; a given paint may endure for long periods in some

places while in other places in the same city it may deteriorate rapidly and become worthless in a comparatively short time. This is due partly, no doubt, to differences of soil conditions. General failure of these paints under conditions where electrolysis was to be expected indicate that the stray currents have much to do with the destruction of the coatings. With a view to throwing further light on this point and also to determine if possible something of the relative value of these coatings as a possible protection against electrolysis, the Bureau of Standards has carried out a considerable number of experiments with different types of commercial pipe coatings and protective paints which have yielded considerable definite information.

(*a*) *Work of Previous Investigators on Paint Coatings.*—A considerable amount of work relating to surface insulation of pipes has been done by many pipe-owning companies as well as in special investigations by individuals. The most extensive work in this direction carried on by individual investigators was that reported by R. B. Harper before the Illinois Gas Association in March, 1909. In this investigation more than 38 different compounds, including paints, dips, and wrappings, were tested. The conclusions given in the report state that no insulating coating was found that would resist the attacks of electrolysis for any considerable length of time. Against the results of these tests, however, there has been directed a criticism that the voltage used on the coatings was abnormally high (110 volts), and therefore would not represent actual working conditions, where the voltage might average but a few per cent of the above value.

This criticism would appear to be more or less well founded, because it is not desirable as a rule to accept an intensive test as conclusive, and this is particularly true in a case where a breakdown voltage may be involved. It is not safe to assume that because a coating will not withstand the action of 110 volts it is therefore not suitable for insulating pipes at 10 volts or less, and since the voltages to which a pipe coating would be subjected under most practical conditions would not exceed a few volts, tests made on 110 volts would not appear to furnish altogether reliable data as to the value of the coatings as a protection against electrolysis.

In addition to the work mentioned in the previous paragraph that of various other investigators also points to the fact that at least a large proportion of the paints sold for the purpose of preserving metals from corrosion are not impervious to water, and as will be shown later this is a vital point in the protection of pipes from electrolytic corrosion by such means. From the standpoint of soil corrosion the access of a slight amount of moisture to the surface of the iron may not be a serious matter, provided the paint is an inhibitor of corrosion, or at least does not form a galvanic couple with the iron, but if there is a difference of potential of even a few volts between the pipes and soil, the results may be very serious, as shown by the experimental data presented later in this paper.

(*b*) *Materials Available for Insulation of Pipes.*—The materials which are commercially available for this particular kind of insulation work and which are practicable commercially may be divided into four general classes:

(1) Paints or compounds which are to be applied at ordinary temperatures, depending on oxidation or other chemical action, drying, etc., for their setting properties.

(2) Dips or compounds intended to be melted at a high temperature and the iron immersed and left until bath and iron are at the same temperature, when the iron is removed and allowed to cool, the compound hardening with decreasing temperature. These dips include asphalts, coal tar, pitches, and allied products.

(3) Wrappings which consist of alternate layers of compound and fabric, the compounds used including the classes mentioned under both (1) and (2), while the fabric may be either felt, cloth, or paper. These may be treated or untreated, according to the ideas of the manufacturer or the person making the test.

(4) Coverings consisting of some sort of conduit, or a large pipe inclosing the pipe or cable to be protected, the intervening space between pipe and conduit being sometimes filled with an insulating material such as pitch.

(*c*) *Tests on Pipe Coatings.*—Coatings of the first three classes—namely, paints, dips, and wrappings—have been tested in considerable number during the course of these investigations. The

details of the experiments thus far completed relating to pipe coverings are reported in full in Technologic Paper No. 15 of the Bureau of Standards, so that only a summary of the results need be presented here.

In making these tests the coatings were carefully applied in accordance with instructions of the manufacturers, and in all cases a sufficient number of coatings were applied to give perfect continuity and insure the absence of pinholes over the entire surface. In order to determine whether or not there were any flaws in the finished coating, the coated surface was immersed in salt water, and an electromotive force of 80 volts was applied between the coated iron and the salt solution for a period of 30 seconds. A very sensitive milliammeter was placed in series with the electric circuit and gave a deflection in case there was a minute flaw at any point of the coating. After 30 seconds the electromotive force was removed and the electrical resistance of the coating measured by a special method. The coating was then placed under a life test by immersing the coated surface in a suitable electrolyte, usually Potomac River water, and impressing on the coating a low potential difference between the iron and the surrounding water. As a rule, five specimens of each kind were used, in two of which the coated iron was made positive and in one negative, and in the remaining two no electromotive force was applied. The electromotive force permanently applied during the life test was 4 volts in all cases for the painted pipes and 15 volts in the case of the dips and wrappings.

Table 1 gives the condensed data for the tests on the pipes covered by paint coatings. This table shows the number of coatings given each specimen, the resistance in ohms per square centimeter before the test was started, the electrolyte used, which in most cases was water from city mains, and the voltage of the time test. The polarity of the coated iron, hours elapsing before the first appearance of current flow in positive, negative, and neutral specimens, and the weeks of drying prior to testing are also given for each specimen.

TABLE 1

Tests of Metal-Preservative Paints as Insulating Coatings

Paint No.	Name of paint	Specimen	Coats	Resis., ohms per cm[a]	Electrolyte	Voltage of time test	Polarity of cone	Hours to failure			Weeks of drying
								Pos.	Neg.	Neut.	
1	Antakwa, heavy.....	1	4	2.0 x 10^{11}	2% Na_2CO_3...	4	Pos...	312	.....	.....	2
		2	4	2.0 x 10^{11}	Water.....	4	Pos...	384	.....	.....	2
		3	4	>2.0 x 10^{11}	.....do.....	4	Neg...	.....	2000	.....	8
		4	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	1400	8
		5	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	1400	8
2	Antakwa, metal protection.	1	4	2.0 x 10^{11}	2% Na_2CO_3...	4	Pos...	192	.....	.....	2
		2	4	1.6 x 10^{9}	Water.....	4	Pos...	0	.....	.....	2
		3	4	>2.0 x 10^{11}	.....do.....	4	Neg...	.....	2000	.....	8
		4	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	1400	8
		5	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	1400	8
3	R. I. W., number not known.	1	4	2.0 x 10^{11}	½% H_2SO_4.....	4	Pos...	312	.....	.....	2
		2	4	>2.0 x 10^{11}	Water.....	4	Pos...	5000	.....	.....	2
		3	4	>2.0 x 10^{11}	.....do.....	4	Neg...	.....	600	.....	8
		4	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	600	8
		5	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	1350	8
4	Carbonkote, interior	1	4	3.0 x 10^{10}	½% H_2SO_4.....	4	Pos...	528	.....	.....	2
		2	5	3.6 x 10^{10}	Water.....	4	Pos...	(a)	.....	.....	2
		3	4	>2.0 x 10^{11}	.....do.....	4	Neg...	.....	(a)	.....	8
		4	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	(a)	8
		5	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	(a)	8
5	Mindura, brine-resisting finish.	1	5	7.0 x 10^{9}	3% NaCl.....	4	Pos...	840	.....	.....	2
		2	5	3.2 x 10^{9}	Water.....	4	Pos...	120	.....	.....	2
		3	5	>2.0 x 10^{11}	.....do.....	4	Neg...	.....	760	.....	8
		4	5	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	570	8
		5	5	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	570	8
6	Mindura, ordinary finish.	1	5	10.8 x 10^{9}	2% Na_2CO_3....	4	Pos...	5	.....	.....	2
		2	5	3.2 x 10^{9}	Water.....	4	Pos...	7	.....	.....	2
		3	5	>2.0 x 10^{11}	.....do.....	4	Neg...	.....	2000	.....	8
		4	5	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	2800	8
		5	5	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	2800	8
7	Nev-a-Rust.....	1	4	1.7 x 10^{9}	2% Na_2CO_3....	4	Pos...	5	.....	.....	2
		2	4	7.7 x 10^{8}	Water.....	4	Pos...	240	.....	.....	2
		3	4	1.6 x 10^{9}	.....do.....	4	Neg...	.....	120	.....	8
		4	4	1.6 x 10^{9}	.....do.....	0	Neut..	.....	.....	336	8
		5	4	2.1 x 10^{9}	.....do.....	0	Neut..	.....	.....	902	8
8	Carbonall, No. 10...	1	4	2.0 x 10^{10}	½% H_2SO_4.....	4	Pos...	5	.....	.....	2
		2	4	5.5 x 10^{10}	Water.....	4	Pos...	552	.....	.....	2
		3	4	>2.0 x 10^{11}	.....do.....	4	Neg...	.....	3144	.....	8
		4	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	1100	8
		5	4	>2.0 x 10^{11}	.....do.....	0	Neut..	.....	.....	1100	8
9	Carbonkote, No. 100.	1	4	3.0 x 10^{9}	2% Na_2CO_3...	4	Pos...	72	.....	.....	2
		2	5	1.6 x 10^{9}	Water.....	4	Pos...	1368	.....	.....	8
		3	4	1.1 x 10^{11}	.....do.....	4	Neg...	.....	6000	.....	8
		4	4	1.1 x 10^{11}	.....do.....	0	Neut..	.....	.....	2800	8
		5	4	5.5 x 10^{10}	.....do.....	0	Neut..	.....	.....	2800	8
10	Sarco.....	1	4	2.0 x 10^{11}	½% H_2SO_4....	4	Pos...	312	.....	.....	2
		2	4	3.4 x 10^{7}	Water.....	4	Pos...	0	.....	.....	8
		3	4	9.2 x 10^{6}	.....do.....	4	Neg...	.....	1752	.....	8
		4	4	1.2 x 10^{8}	.....do.....	0	Neut..	.....	.....	336	8
		5	4	1.0 x 10^{6}	.....do.....	0	Neut..	.....	.....	336	8
11	AeOnite, preservative paint.	1	4	4.5 x 10^{8}	.....do.....	4	Pos...	5	.....	.....	2
		2	4	3.6 x 10^{8}	.....do.....	4	Pos...	0	.....	.....	2
		3	4	6.2 x 10^{9}	.....do.....	4	Neg...	.....	2952	.....	8
		4	4	5.4 x 10^{9}	.....do.....	0	Neut..	.....	.....	336	8
		5	4	5.6 x 10^{9}	.....do.....	0	Neut..	.....	.....	1208	8

[a] No sign of current after 10,000 hours.

TABLE 1—Continued

Paint No.	Name of paint	Specimen	Coats	Resis., ohms per cm	Electrolyte	Voltage of time test	Polarity of cone	Hours to failure			Weeks of drying
								Pos.	Neg.	Neut.	
12	Crysolite, No. 10	1	4	1.0×10^{9}	Water	4	Pos	0			2
		2	4	6.6×10^{9}	do	4	Pos	240			2
		3	4	$>2.0 \times 10^{11}$	do	4	Neg		860		8
		4	4	1.1×10^{11}	do	0	Neut			1300	8
		5	4	1.1×10^{11}	do	0	Neut			600	8
13	Neponset, Waterdyke paint.	1	4	1.2×10^{9}	do	4	Pos	0			2
		2	5	$>2.0 \times 10^{11}$	do	4	Pos	2800			2
		3	4	1.1×10^{9}	do	4	Neg		10000		8
		4	4	3.5×10^{7}	do	0	Neut			1752	8
		5	4	9.2×10^{8}	do	0	Neut			2376	8
14	No. 107, H. F. Scott	1	4	1.0×10^{10}	do	4	Pos	5			2
		2	4	2.2×10^{9}	do	4	Pos	6500			8
		3	4	1.8×10^{8}	do	4	Neg		912		8
		4	4	6.8×10^{9}	do	0	Neut			912	8
		5	4	2.0×10^{7}	do	0	Neut			3200	8
15	Insulite	1	4	1.0×10^{6}	do	4	Pos	10000			8
		2	5	2.2×10^{9}	do	4	Pos	48			2
		3	4	$>2.0 \times 10^{11}$	do	4	Neg		2700		2
		4	4	4.2×10^{7}	do	0	Neut			336	8
		5	4	1.8×10^{7}	do	0	Neut			336	8
16	Bar-OX	1	4	1.5×10^{9}	do	4	Pos	3300			8
		2	4	1.6×10^{9}	do	4	Pos	816			8
		3	4	1.6×10^{9}	do	4	Neg		206		8
		4	4	3.7×10^{10}	do	0	Neut			700	8
		5	4	3.7×10^{10}	do	0	Neut			1400	8
17	R. I. W., No. 5	1	4	5.0×10^{10}	do	4	Pos	1320			8
		2	4	5.6×10^{9}	do	4	Pos	480			8
		3	4	3.9×10^{9}	do	4	Neg		3900		8
		4	4	$>2.0 \times 10^{11}$	do	0	Neut			1400	8
		5	4	$>2.0 \times 10^{11}$	do	0	Neut			1400	8
18	Gliddens, acid proof and graphite acid proof.	1	4	5.0×10^{10}	do	4	Pos	4500			8
		2	4	2.5×10^{10}	do	4	Pos	5300			8
		3	4	2.5×10^{10}	do	4	Neg		2800		8
		4	4	8.5×10^{10}	do	0	Neut			2880	8
		5	4	1.0×10^{5}	do	0	Neut			2800	8
19	Hydrex, preservative paint.	1	4	4.6×10^{9}	do	4	Pos	2600			8
		2	4	8.4×10^{9}	do	4	Pos	816			8
		3	4	$>2.0 \times 10^{11}$	do	4	Neg		2600		8
		4	4	2.5×10^{7}	do	0	Neut			912	8
		5	4	4.3×10^{7}	do	0	Neut			912	8
20	R. I. W., No. 49, over Tockolith.	1	3	7.2×10^{9}	do	4	Pos	192			8
		2	3	7.2×10^{9}	do	4	Pos	192			8
		3	3	5.6×10^{9}	do	4	Neg		100		8
		4	3	$>2.0 \times 10^{11}$	do	0	Neut			1600	8
		5	3	$>2.0 \times 10^{11}$	do	0	Neut			2000	8
21	Insulate	1	4	$>2.0 \times 10^{11}$	do	4	Pos	100			8
		2	4	$>2.0 \times 10^{11}$	do	4	Pos	1586			8
		3	4	3.1×10^{9}	do	4	Neg		2800		8
		4	4	$>2.0 \times 10^{11}$	do	0	Neut			1200	8
		5	4	4.2×10^{9}	do	0	Neut			900	8
[a]22	Insulator, Carman	[b]1	4	4.0×10^{6}	do	4					
		2	4		do						
		3	4		do						
		4	4		do						
		5	4		do						

[a] Four holes eaten through cone in 48 hours. Ten specimens in all were required to obtain one which would withstand the first test. All were carefully treated and dried 8 weeks.

[b] Nos. 2 to 5 failed on 80 volts.

TABLE 1—Continued

Paint No.	Name of paint	Specimen	Coats	Resis., ohms per cm	Electrolyte	Voltage of time test	Polarity of cone	Hours to failure			Weeks of drying
								Pos.	Neg.	Neut.	
[a]23	Damp-proofer, Carman.	[b]1	4	1.2×10^{8}	Water	....	.....	.....	.....	.....	....
		2	4	.....	....do	....	.....	.....	.....	.....	....
		3	4	.....	....do	....	.....	.....	.....	.....	....
		4	4	.....	....do	....	.....	.....	.....	.....	....
		5	4	.....	....do	....	.....	.....	.....	.....	....
24	Crysolite, No. 8	1	4	$>2.0 \times 10^{11}$	....do	4	Pos	150	.....	.....	8
		2	4	7.0×10^{8}	....do	4	Pos	1032	.....	.....	8
		3	4	1.0×10^{6}	....do	4	Neg	.....	120	.....	8
		4	4	1.0×10^{6}	....do	0	Neut	.....	.....	1032	8
		5	4	1.0×10^{6}	....do	0	Neut	.....	.....	1032	8
25	Dixon's graphite	1	5	9.0×10^{7}	....do	4	Pos	48	.....	.....	2
		2	4	3.3×10^{8}	....do	4	Pos	2800	.....	.....	2
		3	4	1.6×10^{9}	....do	4	Neg	.....	120	.....	8
		4	4	1.6×10^{9}	....do	0	Neut	.....	.....	120	8
		5	4	1.8×10^{8}	....do	0	Neut	.....	.....	120	8
26	S. P. C., flexible iron paint.	1	4	1.2×10^{8}	....do	4	Pos	96	.....	.....	8
		2	4	2.3×10^{7}	....do	4	Pos	0	.....	.....	8
		3	4	1.8×10^{8}	....do	4	Neg	.....	10000	.....	8
		4	4	1.0×10^{8}	....do	0	Neut	.....	.....	672	8
		5	4	2.2×10^{8}	....do	0	Neut	.....	.....	672	8
27	P & B, No. 2	1	4	9.8×10^{7}	....do	4	Pos	6500	.....	.....	8
		2	4	2.0×10^{8}	....do	4	Pos	912	.....	.....	8
		3	4	2.0×10^{7}	....do	4	Neg	.....	288	.....	8
		4	4	2.9×10^{8}	....do	0	Neut	.....	.....	912	8
		5	4	1.0×10^{4}	....do	0	Neut	.....	.....	912	8
[c]28	P & B, black, air-drying varnish.	1	4	.....	....do	4	Pos	96	.....	.....	8
		2	4	.....	....do	4	Pos	96	.....	.....	8
		3	4	.....	....do	4	Neg	.....	96	.....	8
		4	4	.....	....do	0	Neut	.....	.....	6500	8
		5	4	.....	....do	0	Neut	.....	.....	6500	8
29	National, double K natural graphite paint.	1	4	4.0×10^{8}	....do	4	Pos	10000	.....	.....	8
		2	4	3.4×10^{8}	....do	4	Pos	10000	.....	.....	8
		3	4	3.4×10^{8}	....do	4	Neg	.....	912	.....	8
		4	4	3.4×10^{8}	....do	0	Neut	.....	.....	912	8
		5	4	3.4×10^{8}	....do	0	Neut	.....	.....	912	8
30	Des Moines, elaterite, No. 40.	1	4	2.7×10^{8}	....do	4	Pos	10000	.....	.....	8
		2	4	2.2×10^{8}	....do	4	Pos	10000	.....	.....	8
		3	4	1.8×10^{8}	....do	4	Neg	.....	120	.....	8
		4	4	6.0×10^{7}	....do	0	Neut	.....	.....	2440	8
		5	4	4.0×10^{8}	....do	0	Neut	.....	.....	2000	8
31	Des Moines, elaterite, No. 10.	1	4	9.7×10^{6}	....do	4	Pos	120	.....	.....	8
		2	4	2.1×10^{7}	....do	4	Pos	3300	.....	.....	8
		3	4	4.0×10^{6}	....do	4	Neg	.....	120	.....	8
		4	4	1.8×10^{7}	....do	0	Neut	.....	.....	96	8
		5	4	9.7×10^{6}	....do	0	Neut	.....	.....	96	8
32	I. D. P., steel paint	1	4	4.0×10^{6}	....do	4	Pos	120	.....	.....	8
		2	4	6.5×10^{7}	....do	4	Pos	120	.....	.....	8
		3	4	6.0×10^{7}	....do	4	Neg	.....	120	.....	8
		4	4	5.7×10^{7}	....do	0	Neut	.....	.....	96	8
		5	4	1.0×10^{6}	....do	0	Neut	.....	.....	96	8
							Av.=	1647	—2900	3112	

[a] Five holes eaten through cone in 48 hours. Ten specimens in all were required to obtain one which would withstand the first test. All were carefully treated and dried 8 weeks

[b] Nos. 2 to 5 failed on 80 volts.

[c] Resistance very low, about 1,000 ohms.

The general appearance of the data under the columns "Hours to failure," which is of course the most important, indicates that a paint is not to be depended upon as a preventive of electrolysis in the presence of moisture, even though the voltage between the pipes and earth be only 4 volts. Here and there an individual specimen appears which seems to have withstood the action of the water for a considerable period of time, and in coating No. 4 only one of the four specimens has been broken down after a little more than a year. It may be said of No. 4, therefore, that it gives far greater promise of good results in practice than any of the others.

The average of the hours to failure seems to indicate that positive specimens lose their insulating power first, with negative specimens second, and those not subjected to a difference of potential third; but the differences are too small to be conclusive on this point. On the contrary, an examination of the data, specimen by specimen, shows quite clearly that the low electric stress applied had very little effect toward reducing the insulation resistance of the paint. The time of the breakdown evidently depends more upon characteristics of the individual specimens than on the action of the water. The manner in which failure of the coating occurred depended upon the direction of current flow.

The anode specimens showed rust spots at the places where the breakdown first took place. These rust spots would grow to craters in some places if the paint coating was brittle and easily broken, or bubbles would form if the coating was elastic. The removal of this crater or bubble would reveal a pit filled with iron rust, the pits in time extending clear through to the sheet iron. The cathode specimens failed in an entirely different way. No rusting of the iron occurred under the paint coating, but gas was liberated, which lifted the film until a blister was formed which would sometimes break and leave a large area of iron exposed. These forms of failure are illustrated in Fig. 5, the specimen on the right being the anode specimens, while the one on the left is a cathode specimen. The specimens having no electromotive force applied showed no deterioration of the coating which was visible to the eye, except in one or two cases where the paint blistered somewhat, as it did when the specimens were made cathode. Coating No. 6 showed this type of failure in the greatest degree.

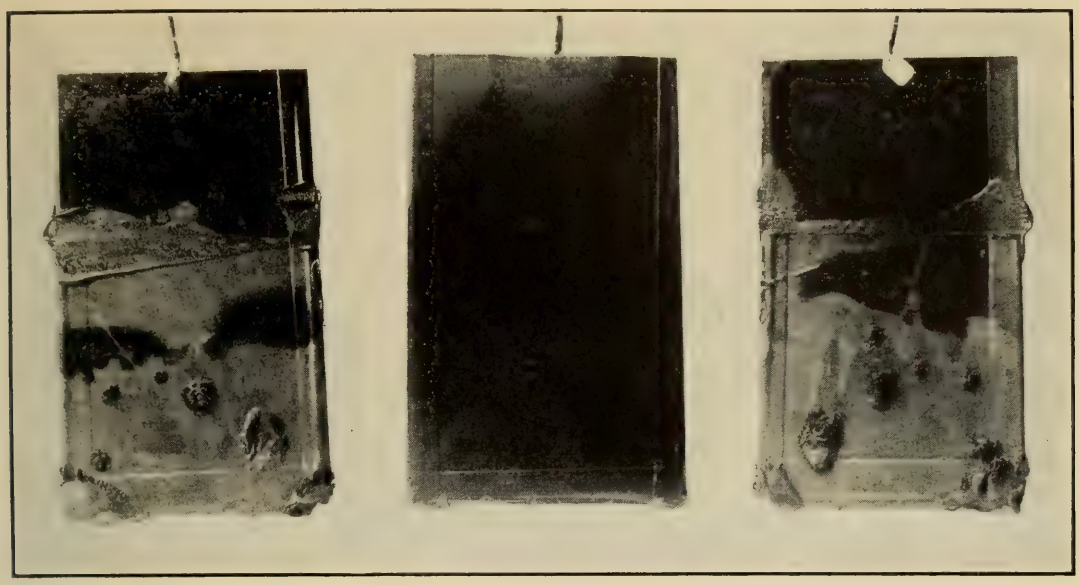


FIG. 5.—*Showing characteristic failure of paint coatings*

FIG. 6.—*Showing pittings on coated pipes*

It is evident from the rapid failure of practically all of these coatings that they can not be depended upon even for a few months effectually to protect buried pipes from electrolysis due to stray currents.

The tests on pipes covered with dips and wrappings show somewhat more favorable results. The data on these tests are given in the following table:

TABLE 2.

Tests of Pipe Wrappings, Dips, Etc., as Insulating Coatings

[Water served as electrolyte in all cases. Voltage=15 except in 1–1 and 4–1 where V=4, and also 206 to 225]

Coating	Material	Layers or dippings	Specimen	Polarity of cone	Hours to failure	
					Positive	Negative
1	Neponset water-dyke felt and compound	3 layers	1	Positive	9200	
			2	do	5040	
			3	do	6000	
			4	Negative		2160
			5	do		9200
2	do	2 layers	9	Positive	7600	
			10	do	4200	
			11	Negative		3600
			12	do		10000
3	do	1 layer	17	Positive	10000	
			18	do	10000	
			19	Negative		3100
			20	do		4200
4	Hydrex felt and compound	3 layers	25	Positive	16000	
			26	do	14700	
			27	do	[a]14000	
			28	Negative		3200
			29	do		5000
5	do	2 layers	33	do		2000
			34	do		2900
			35	Positive	10000	
			36	do	10000	
6	do	1 layer	41	Negative		3040
			42	do		2000
			43	Positive	10000	
			44	do	3800	
7	Pitch and burlap	3 layers	49	do	14700	
			50	Negative		4300
8	do	2 layers	51	Positive	5700	
			52	Negative		5000
9	Barrett specification pitch and tar paper	3 layers	57	Positive	3500	
			58	do	4800	
			59	Negative		3900
			60	do		2100

[a] No failure after the given number of hours.

TABLE 2—Continued

Coating	Material	Layers or dippings	Specimen	Polarity of cone	Hours to failure	
					Positive	Negative
10	Barrett specification pitch and tar paper	2 layers	65	Positive	2100	
			66	do	2100	
			67	Negative		720
			68	do		720
11	do	1 layer	73	Positive	3400	
			74	do	3400	
			75	Negative		552
			76	do		48
12	Barrett pitch (sample 1) and muslin	3 layers	81	Positive	12500	
			82	do	3400	
			83	Negative		3900
			84	do		3900
13	Barrett pitch (sample 2) and muslin	do	89	Positive	12500	
			90	do	12500	
			91	Negative		5500
			92	do		3400
14	Barrett pitch (sample 3) and muslin	do	97	Positive	4400	
			98	do	4400	
			99	Negative		1400
			100	do		3000
15	Barrett pitch (sample 4) and muslin	do	105	Positive	12000	
			106	do	[a] 12000	
			107	Negative		[a] 12000
			108	do		12000
16	Sarco-mineral rubber-pipe dip and muslin	4 layers	113	do		2100
			114	do		2100
			115	Positive	10000	
			116	do	10000	
17	do	3 layers	121	Negative		1400
			122	do		336
			123	Positive	10000	
			124	do	2100	
18	do	2 layers	129	Negative		1200
			130	do		300
			131	Positive	300	
			132	do	2900	
19	do	1 layer	137	Negative		2100
			138	do		300
			139	Positive	300	
			140	do	2100	
20	Mogul repairing compound and muslin	2 layers	145	do	1600	
			146	do	1600	
			147	Negative		1600
			148	do		1000
21	do	1 layer	154	Positive	768	
			155	do	1600	
			156	Negative		1600
			157	do		1000

[a] No failure after the given number of hours.

TABLE 2—Continued

Coating	Material	Layers or dippings	Specimen	Polarity of cone	Hours to failure	
					Positive	Negative
22	S. P. Co. cold cementing compound and treated burlap	3 layers	162	Positive	7200	
			163	do	[a] 7200	
			164	Negative		7200
			165	do		7200
23	do	2 layers	170	Positive	[a] 7200	
			171	do	7200	
			172	Negative		480
			173	do		7200
24	do	1 layer	178	Positive	[a] 7200	
			179	do	[a] 7200	
			180	Negative		7200
			181	do		[a] 7200
25	S. P. Co. cementing compound (grade A) and treated burlap	3 layers	186	Positive	[a] 7200	
			187	do	[a] 7200	
			188	Negative		[a] 7200
			189	do		[a] 7200
26	do	2 layers	194	Positive	[a] 7200	
			195	do	[a] 7200	
			196	Negative		[a] 7200
			197	do		[a] 7200
27	do	1 layer	202	Positive	[a] 7200	
			203	do	7200	
			204	Negative		[a] 7200
			205	do		7200
28	Sarco-mineral rubber-pipe dip	2 dippings	206	Positive	24	
			207	do	5	
			208	do	96	
			209	do	9000	
29	Barrett pitch (sample 1)	do	210	do	0	
			211	do	0	
			212	Negative		360
			213	do		0
30	Barrett pitch (sample 2)	do	214	Positive	336	
			215	do	0	
			216	Negative		0
			217	do		1056
31	Barrett pitch (sample 3)	do	218	Positive	672	
			219	do	4400	
			220	Negative		1680
			221	do		4400
32	Barrett pitch (sample 4)	do	222	Positive	0	
			223	do	6000	
			224	Negative		672
			225	do		336
33	Minwax and cloth	2 layers	226	Positive	[a] 3192	
			227	do	[a] 3192	
			228	Negative		[a] 3192
			229	do		[a] 3192

[a] No failure after the given number of hours.

It is seen from this table that 82 per cent of the total number of specimens under test had failed after the tests had been in progress about 7200 hours. Coatings Nos. 25, 26, and 33 seem to remain intact, but they were among the last ones put in circuit, so their behavior had not been definitely determined when it became necessary to discontinue the tests. No. 27, however, which is of the same material as 25 and 26, shows two individual specimens which have broken down. These are of one layer of compound and burlap, and it seems reasonable to say that they forecast the future behavior of the others of the same material, but having a greater number of coatings. The results taken as a whole do not indicate that the life of insulating coatings of this character can be expected to be more than two or three years, even when carefully put on the pipes and buried in perfect condition; in most cases failure may be expected to occur within a few months.

The attempts to dip specimens appear to have yielded very poor results, and it is questionable whether coating pipes in this way is any better than painting. The manner of failure of the coatings was similar to that of the paint coatings described above. Failure of the covering was much slower than in the case of the paint coatings after the first appearance of current flow. This is probably due to the greater thickness and rigidity of the coatings.

The characteristic failure of the coating is very strikingly shown in Fig. 5. Explanation of the phenomenon lies in the fact that none of the paints tested are absolutely impervious to moisture, and when they are brought into the presence of water a slight trace of moisture ultimately permeates the coating. When this occurs at any point the coating becomes slightly conducting, and if an electromotive force is applied, a trace of current flows; this gives rise to slight electrolysis, which is accompanied by the formation of more or less gas beneath the coating.

As a rule much more gas is formed if the iron surface is cathode than if anode, so that when current once begins to flow the formation of craters or bubbles in the coating takes place more rapidly if the iron be negative than if it be positive. As this gas increases in volume and expands, the coating is ruptured, after which the current flow is greatly increased at the point of breakdown; in

case the pipes are positive rapid electrolysis of the exposed portion follows. In some cases if the coating is sufficiently porous to permit the gases to escape they remain intact and electrolysis may continue beneath the coating, eating through the metal with little or no superficial evidence of failure of the paint. This phenomenon is frequently observed in pipes in actual practice.

The vital weakness of all paints and wrappings thus far tested is due to the fact that they are not entirely nonabsorbent. If a paint could be secured which is absolutely impervious to soil moisture and which would remain so for an indefinite period of time, it would prove an effective preventive of electrolysis; all efforts to produce such paint should be directed to this one end of making it absolutely and permanently moisture proof.

A considerable number of tests were also made on wrapped pipes buried in earth. A number of these pipes were coated by a method in use by a gas company in a large western city, and the specimens actually tested were supplied by the company in question. A considerable number of others were supplied by a large manufacturer of iron and steel pipe, the coatings having been put on primarily for the purpose of reducing soil corrosion. When the pipes were removed from the earth after the test and the wrappings stripped off they were found to be covered with rust spots and here and there were pits of considerable depth. An illustration of these pits is given in Fig. 6. The pipe longest in the ground had been buried about one and a half years, and in that time pits were formed extending almost through the iron. The currents were not large, but the high-current densities resulting from the local failure of the coating resulted in very rapid corrosion of the iron wherever a failure occurred. The test voltage on these buried pipes was about 4½ volts, a voltage of the order of magnitude frequently encountered in practice.

The protection of pipes by laying them in conduit filled with pitch would appear to be effective for a much greater length of time, and in special cases this method would be useful; but the expense would be high if used on a large scale, and at present it appears very questionable whether or not the protection secured would be worth the cost. A large amount of work needs to be done in this direction before definite results on this subject will

be available. As far as paints, dips, and wrappings are concerned, however, there can be no question but that as they are at present applied they are not only of no value when applied only in the positive areas, but they may do actual harm by concentrating the current discharge on a comparatively small portion of the pipe surface, thus giving rise to rapid pitting. On the other hand, such coatings are unquestionably of great value in preventing self-corrosion in the case of pipes not subject to electrolysis from stray currents.

Further, in cities where electrolysis is taking place, if such coatings are placed on the pipes in the negative or neutral areas, they would not only protect against self-corrosion, but owing to the increased resistance between pipes and earth the current which would be picked up by the pipes would be greatly reduced, and electrolysis in the remote positive areas would be correspondingly reduced. It may be said, therefore, that such coatings should never be used in the positive districts where the pipes tend to discharge current into the earth; but they may, if circumstances justify, be applied in the neutral or negative areas. However, for reasons pointed out later in this report, such protection from electrolytic corrosion as might be obtained by the use of these coatings in negative areas should be regarded as of an auxiliary character, to be ultimately superseded by more effective mitigative measures along the lines suggested in a later part of this paper.

2. CHEMICAL PROTECTION

The corrosion of iron due to discharge of electric current is dependent not alone on the amount of the current discharge, but also to a very large extent on the chemical nature of the medium into which the discharge takes place and on a number of other factors. The results of a great many experiments carried out by the Bureau of Standards [3] show that in case of ordinary street soils the amount of corrosion of iron per ampere hour varies considerably with the chemical composition of the soil and also with the physical properties of the soil, such as moisture content, temperature, density, etc.

[3] Burton McCollum and K. H. Logan, "Electrolytic Corrosion of Iron in Soils," Technologic Paper No. 25.

Certain chemicals, as, for example, soluble hydroxides, tend to render iron passive—that is, prevent the corrosion of iron when it is made anode—whereas other chemicals, particularly the chlorides and sulphates, have the opposite tendency. Partly as the result of such opposing tendencies the "coefficient of electrolytic corrosion," or amount of corrosion of the iron which actually takes place in a given soil expressed as a fraction of the theoretical amount, according to Faraday's law, varies between wide limits. Moderately strong solutions of sodium, potassium, or calcium hydroxides alone will entirely prevent the corrosion of the iron by electric currents, and attempts have been made to prevent electrolysis under practical conditions by this means. Sodium and potassium hydroxides are obviously not well suited for this purpose because of their great solubility, which would cause them to diffuse and disappear very quickly. Calcium hydroxide or ordinary hydrated lime is much less soluble, and a soil thoroughly saturated with lime will remain so for a considerable length of time unless soil conditions are such that an abnormal amount of seepage occurs. This material has therefore been used in the attempts that have been made to prevent electrolysis by this method.

We have found, however, that while a saturated solution of lime will, when practically pure, completely prevent electrolysis with ordinary current densities, it loses its power entirely when mixed with any considerable amounts of certain salts, such as chlorides, sulphates, carbonates, etc., which occur to a greater or less extent in practically all soils, and which always tend to concentrate about an electrode discharging current into the soil. The protection afforded to pipes by laying them in lime, therefore, is of a transient character, and with the diffusion of the earth salts into the lime its protective property ultimately disappears. The temporary protection afforded by this means is too short lived to justify the expense of its application, except, perhaps, in very special cases where conditions are peculiarly suited to its use.

3. CEMENT COATINGS

Cement coatings have been used on pipes for many years, and the claim has been made, and is still made, by certain manufacturers of cement-lined and cement-coated pipes that their product

is immune from electrolysis. In so far as we have been able to observe, however, in all those cases in which these pipes have withstood moderately severe electrolysis conditions without injury for any considerable length of time the pipes have also been laid with cement joints, and it appears certain that the immunity which has been claimed for these pipes has been due to the high resistance joints rather than to the cement coatings. This conclusion is borne out by the results of tests which we have made on experimental lines of these cement-covered pipes on the grounds of the Bureau of Standards. Two experimental lines of these pipes were laid 20 feet apart, one being laid with calked lead joints and the other with cement joints. These were subjected to identical conditions, such as would under ordinary conditions give rise to considerable electrolysis. After about two years excavation revealed the fact that the line having lead joints had already suffered considerably from electrolysis, while the one having cement joints showed practically no evidence of trouble.

From theoretical considerations we might expect that a cement covering would exert a temporary protective influence, since the cement contains a considerable amount of lime, and, as pointed out above, this has a tendency to prevent corrosion of the iron. In fact we have repeatedly demonstrated that iron pipes embedded in cement and kept free from contaminating influences will not corrode to any great extent, even when discharging current at densities which are usually found in the case of underground pipes in practice. When, however, a pipe is covered with a layer of cement an inch or so in thickness and buried in the earth, it requires but a comparatively short time for the earth salts to diffuse into the cement, particularly if the pipes be discharging currents into the earth. This migration of the negative ions into the cement is due largely to the flow of electric current, the negative ions migrating in all cases in the opposite direction from that in which the current is flowing.

As a result of this entrance into the cement of the acid radicals contained in the soil, the protective effect of the calcium hydroxide is in time destroyed.

It has been claimed by some that the resistance of a cement coating is enough higher than the resistance of earth to bring

about a material reduction in the current flow to and from the pipes. Our experiments regarding this point do not, however, bear out this claim. We have found that the specific resistance of water-soaked cements, mortars, and concrete will vary as a rule from 2,000 to 8,000 ohms per centimeter cube, which is but little greater than the average specific resistance of a large number of samples of soil obtained from a number of widely scattered cities throughout the country. Further, experiments described, in Technological Paper No. 18 of the Bureau of Standards show that if a small amount of corrosion occurs under the cement coating the expansive forces which develop will shortly cause cracking and splitting off of the cement. We are, therefore, convinced that the protective effect of cement coatings, like that obtained by burying pipes in lime, is but a temporary one and can not be seriously considered as a practical means of permanent electrolysis mitigation.

4. CATHODIC PROTECTION

Since corrosion of pipes occurs only where the current flows from the pipes into the earth, it is obvious that if we could devise some means of always maintaining the pipes negative to the earth at all points of the system electrolysis could not occur. A great many attempts have been made to utilize this principle, and a number of patented methods of electrolysis prevention are based upon it.

Broadly speaking, the principle of cathodic protection involves also another factor in addition to keeping the current always flowing toward the pipes. In some systems where this protection has been proposed, efforts have been made to produce and maintain a passive state of the iron by the production and concentration of alkali, which, under certain circumstances, takes place at a cathodic surface. One method that has been proposed for accomplishing this consists essentially in impressing an unsymmetrical alternating current on the pipe system in such a way as to make the average unidirectional current approximately zero. Under certain soil conditions this alternating current will produce a strong hydroxide solution in the soil adjacent to the pipes, which would tend to produce a passive condition of the iron, tending to protect it from corrosion.

The objections to this latter system are several. In the first place the apparatus required for automatically maintaining a proper unsymmetrical alternating current flow into the pipes involves considerable complication and expense. In the second place it is only under certain soil conditions that a sufficient amount of alkali could be produced to induce the passive state in the iron, and consequently in most cases protection by this method would not be had. In the third place even if those conditions under which strong alkalinity in the soil could be produced, a serious danger would be introduced because of the tendency of such alkaline soils to attack lead service pipes forming a part of the system, or the lead sheaths of power and telephone cables. We have no hesitation in saying that the system would not only be ineffective in most cases but would actually become a menace in others, and it is therefore not to be considered seriously as a means of electrolysis mitigation.

Another method of applying cathodic protection, and the one most commonly thought of when such protection is proposed, consists in connecting a low-voltage generator between the pipe system to be protected and the adjoining rails in each positive area, and so exciting this generator as to maintain the pipes always at a lower potential than the rails. This is very closely related to certain forms of the common pipe-drainage system described below and possesses all of the disadvantages of the latter together with the additional drawbacks of extra expense and complication. At the same time it appears to offer no material advantage over the usual types of pipe-drainage system.

A patented modification of the above method that has been developed abroad consists in substituting a large metallic electrode buried in the earth for the tracks as the positive electrode, the pipe system being as before maintained negative to earth. This plan of substituting a buried electrode for the tracks as the positive terminal has two marked disadvantages, namely, the increased cost of providing the electrode and the relatively small radius of the protected zone. Experiments carried out by us show that the extent of the region protected depends very much on the size of the buried positive electrode and also to a large extent on its position with respect to the pipe system.

Figure 7 shows in diagrammatic form a layout of experimental pipe lines used for studying this problem. Two parallel pipe lines (*D* and *E*, Fig. 7) were buried about 20 feet apart, one of 4-inch cast-iron pipe and the other a 3-inch steel pipe. Between these pipe lines a 5-volt battery, *F*, was connected in such a way as to make the cast-iron pipe positive, so that it would tend to discharge current into the earth and thence to the steel pipe. A motor generator set was then connected between the pipe line *D* and one of the small buried electrodes *A*, *B*, *C*, the connection being such as to cause current to flow from the buried electrode *A*, for example, into the earth and thence into the pipe line *D*. It will be seen, therefore, that the small 5-volt battery *F* tends to cause current flow from the pipe line *D* into the soil; whereas the motor generator set *G* tends to cause current to flow into the pipe line *D*. The motor generator set, therefore, tends to protect the pipe line *D* from corrosion by the current from the battery *F*, and if the protective tendency of the motor generator set could be made everywhere sufficiently great, it would entirely prevent corrosion of the protected pipe.

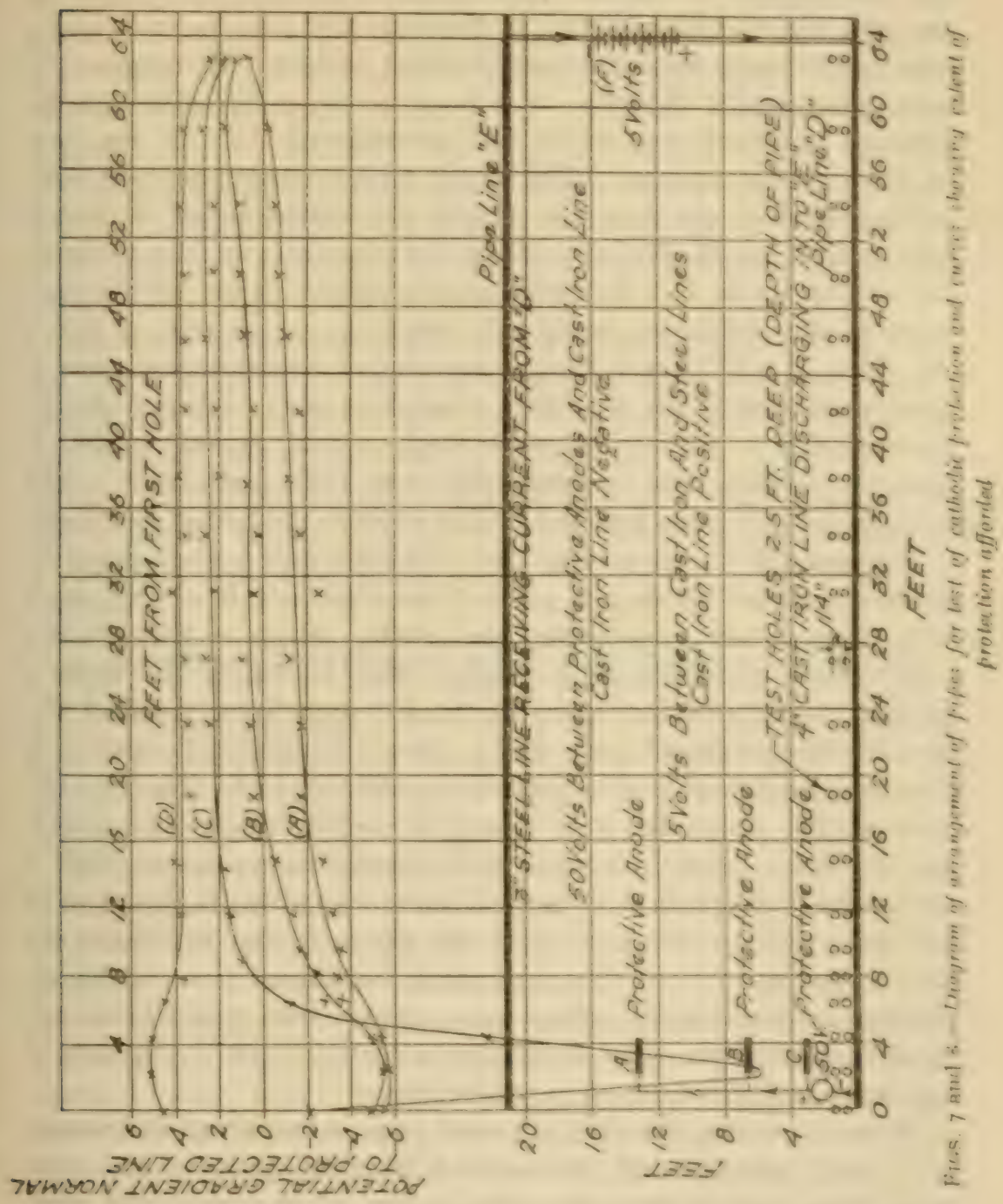
In order to determine to what extent such protective tendency existed, careful exploration was made throughout a considerable length of the pipe line *D* in order to ascertain to what points and to what extent it was discharging current into the earth under various connections of the protecting motor generator set *G*. In order to make these explorations a series of holes *H* were drilled in the ground immediately beside the pipe line *D*. These holes were drilled in pairs to the same depth as that of the pipe. One hole of each pair terminated immediately beside the pipe and the other about a foot farther away. With suitable non-polarizable electrodes the potential difference between the bottoms of the holes of each pair could be measured, and this was, of course, proportional to the surface intensity of the current discharged from the pipe surface assuming uniform soil resistance throughout, which was substantially the case. By measuring the potential difference between the bottoms of the different pairs of holes we could then plot a curve showing the intensity of the current discharged along the length of the pipe.

A series of such measurements were first made with the motor generator set connected between the buried pipe line *D* and the buried electrode *A*. The motor generator set was then connected between *D* and the buried electrode *B*, and the series of measurements on all the holes repeated, after which a similar series of measurements was made with the motor generator set connected between *D* and *C*. The results of these measurements are plotted in curves shown in Fig. 8, shown on the same sheet, both figures being drawn to the same scale. In this figure curve *D* shows the potential difference between the bottoms of the test holes when the motor generator *G* was disconnected entirely—in other words, when there was no tendency whatever to protect the pipe line *D* from corrosion. The ordinates of this curve show roughly, the relative danger of corrosion of the pipe at any point along its length, and it will be seen that the pipe is positive throughout. The motor generator set was then connected between the pipe line *D* and the buried electrode *C*, which was buried at a distance of 40 inches from the pipe line *D*.

It was found necessary in the preliminary experiments to impress about 50 volts from the motor generator set in order to get any appreciable amount of protection even in the immediate vicinity of the buried anode, and this voltage was therefore maintained throughout the test. With the 50 volts impressed between the anode *C* and the pipe line the series of potential measurements between the bottoms of the test holes gave the curve *C*. It will be seen that in the immediate vicinity of the buried anode there is a marked reversal of polarity, the pipe being strongly negative to earth for a distance approximately equal to the length of the anode.

As we proceed along the pipe, however, the negative condition of the pipe diminishes with great rapidity, and at a distance of about 4 feet from the end of the buried anode it will be seen that the pipe has become positive, and as we proceed farther away from the anode along the pipe we find that the pipe becomes more and more strongly positive to the soil until at a distance of about 20 feet from the buried anode the potential of the pipe against the earth is practically the same as it was without the motor generator connected to the anode. The remaining length of the

pipe as far as explored was in practically the same condition. The motor generator set was then connected between the pipe line *D* to the buried anode *B*, which was located at a distance of



Figs. 7 and 8 — Diagram of arrangement of pipes for test of cathodic protection and curves showing extent of protection afforded

80 inches from the pipe line *D*, or twice as far as anode *C*. The series of potential measurements was then repeated and the data plotted as curve *B*.

It will be seen here that the negative condition of the pipe *D* immediately opposite the buried electrode is less pronounced than in the case where the electrode is buried nearer the pipe, but the negative condition persists for a greater distance along the pipe line to be protected, in this case the pipe line remaining negative to earth for a distance of about 18 feet. Throughout its remaining length the pipe was positive to earth, although its positive condition was much less pronounced than in the case of the unprotected pipe. The motor generator set was next connected between the pipe line *D* and the buried anode *A*, which was located about 160 inches from the pipe line, or four times as far as the anode *C*. Potential measurements taken in the bottoms of the test holes under this condition are plotted as curve *A*. Here it will be seen that the extent of the protected zone is greatly increased, the pipe line remaining more or less negative to earth for a distance of more than 50 feet, beyond which it became positive, and consequently very little protection could be expected beyond a hundred feet or so from the buried electrode.

It appears from these tests that making a pipe system negative against a buried anode will protect the pipe only in a very small area immediately surrounding the anode. Even in this present case, where the protecting voltage was 10 times the normal potential difference between the buried pipe lines, we find the area of the protected zone to be almost insignificant, and it is very evident that if the protecting voltage were reduced, the area of the protected zone would be reduced correspondingly. In any actual case it would be impracticable to use so high a protective voltage as was used in these experiments, because of the large expense involved, both for the generator units and for the power wasted, so that the results obtained here, although wholly inadequate to afford any appreciable protection, are nevertheless better than could be expected from any practical application of this method of protection.

When, however, the rails are used as positive terminals instead of a small buried anode, the anode is in effect spread over a very large area, and consequently the radius of the protected zone would be much larger than in the case above considered. It appears, therefore, that these patented modifications involving the use of small buried anodes are without merit.

Another form of cathodic protection consists in burying near the pipes a metal which is electropositive to the pipes, such as zinc, and connecting this metallically to the pipes. This tends to protect a small area of pipe near the point of connection, but from the experiments described above it will be obvious that the radius of the protected zone will be extremely small. It has the further disadvantage that a greater number of such connections are required to protect the pipe line, and the zinc or other protecting metal rapidly wastes away. Further, there is no cheap metal which is electropositive to iron, and the expense of this method is therefore prohibitive, except perhaps in extreme cases.

All of the above modifications which employ a booster to lower the mean potential of the pipes tend to cause increased current flow in the pipes, and they also lower their potential with respect to surrounding structures, thereby increasing the danger to the latter. They are, therefore, open to the same objections as the pipe-drainage system described later in this report, besides being as a rule more complicated and more expensive to install and operate.

5. FAVORABLE LOCATION OF PIPES WITH RESPECT TO TRACKS

The location of pipe lines with respect to tracks has a very important bearing on the danger of electrolysis. In general, it may be said that the farther the pipes are from the tracks the less current they will pick up, and hence the total damage will be correspondingly reduced. A more important matter, however, is the distribution of the discharge, it being desirable as far as practicable to distribute the discharge over as large an area as possible. If the pipe in the positive area be brought near to the tracks at one point, as by crossing immediately under it, the tendency is to concentrate the discharge at that point and thereby cause rapid destruction locally. The location of the pipes is therefore more important within the positive area than outside this zone, although in both cases it is important.

In laying new pipes, or replacing old ones therefore, the pipes should be placed as far as practicable from the rails and the crossing of service pipes under the tracks should be avoided if circumstances permit. Some companies make it their regular

practice in the more densely built up districts to lay mains on both sides of the street, in which case the crossing of services under tracks is rarely necessary. In many cases this is not practicable, however, but something can always be accomplished by laying the pipes as deep as possible where they pass under the tracks. The practice of putting mains immediately under the tracks tends greatly to increase damage by electrolysis and should be avoided wherever possible.

It has been contended by some investigators that it is feasible to eliminate altogether damage by electrolysis by taking precautions to keep all parts of the pipe system more than 4 or 5 feet distant from the railway tracks. This plan has been advocated rather strongly by some European engineers, notably Messrs. J. G. and R. G. Cunliffe,[4] who have concluded from extensive experiments on the resistance of ground plates that the tendency of the earth to short-circuit the pipes is so great that if a pipe line is everywhere more than 4 or 5 feet distant from the tracks it will pick up practically no current from the earth.

We are convinced, however, that this deduction is in error. In the first place, the experiments on which this conclusion was based were carried out on very small ground plates in which, obviously, the greater part of the resistance between the electrodes would be within 2 or 3 feet of the electrodes themselves, because of the relatively small cross section of the path of the current in those parts. If, however, we are dealing with very large electrodes, we find that a large part of the resistance between the electrodes is to be found at points much farther from the electrodes. Consequently, if current is being discharged from a very large electrode, the pipe line would have to be removed much farther from the vicinity in order not to pick up any current from it.

In any actual case, we may consider a railway system as constituting a large network forming a single anode discharging current into the earth, and in such a case we can not apply the conclusions that would be drawn from comparatively small anodes, such as used in the experiments above referred to. On the contrary, our own experiments have convinced us that it is

[4] J. G. and R. G. Cunliffe, "Electric traction vagabond currents," Jour. Inst. of Elec. Eng., Vol 43, p. 449.

wholly impracticable to so locate the pipes that they will not be in danger of picking up considerable amounts of current from the earth under conditions which in the past have usually prevailed in most cities in this country. As evidence of this we may cite the fact that quite frequently when investigating voltage conditions in various cities we have encountered localities where even at a distance of 200 yards from the nearest railway line the potential gradients in the earth were as high as several volts per mile.

It is very obvious that a pipe line placed in earth in which such large potential gradients exist, must of necessity pick up large amounts of current. While, therefore, the method of reducing electrolysis troubles by careful location of the pipe lines can never be more than partly successful, we are nevertheless convinced that a good deal can be accomplished in laying new lines by keeping them as far as practicable from the street railway tracks. The advantage of this, as pointed out above, is more because it tends to distribute the current discharge over a large area than because of actual reduction of current in the pipe systems, although the latter is, of course, of some consequence. The limitations of the method of pipe location are, however, very obvious. The major part of the electrolysis problem has to do with the protection of pipe systems where both the pipes and the tracks are already in place; hence this method should be regarded merely as presenting certain features, of which advantage can and should be taken in special cases, and not as a general method of electrolysis mitigation.

6. CONDUCTING COATINGS

If it were practicable to provide a continuous conducting coating for the pipes which would not corrode under the discharge of electric currents, there would be less need of trying to prevent the flow of current in the pipes. Numerous attempts have been made to utilize this principle in electrolysis mitigation. In general, the aim has been to provide on the surface of the pipe a conducting material which is noncorrodable, and which is in metallic contact with the pipe, the idea being that the current would pass from the pipe to the noncorrodable material by metallic conduction, and thence be discharged into the earth without injury. The difficulties of this method lie in the fact that all noncorrodable metals

available for this purpose are too expensive for commercial application, so that attempts to use this method have necessarily been confined to nonmetallic coatings. Here, however, a difficulty is encountered, owing to the impracticability of maintaining a continuous coating by means of any nonmetallic conducting material.

In one attempt to utilize the method of conducting coatings the iron was covered by a layer of black oxide, either by subjecting it to the well-known Bower-Barff treatment or by various other means. Black oxide is a very good conductor of electricity and is noncorrodable under most soil conditions, and at first sight this method might appear promising. It has, however, two serious drawbacks which combine to make the method utterly ineffective in practice. The first is the fact that it has been impossible to to provide a coating of this kind that was entirely free from cracks or other flaws reaching through the coating to the iron below. The second difficulty is due to the fact that iron oxide is electronegative to iron, and wherever a fault develops in the coating permitting soil waters to enter and make contact with the iron, galvanic action is set up which speedily produces severe pitting in the iron. In fact, it is this phenomenon which is in large measure responsible for the unequal corrosion of iron in practice which results in pitting of the surface. The initial corrosion results in the formation of iron oxides at certain points, and these areas at once become electronegative, forcing the current to discharge elsewhere and thus aggravating the rate of deterioration of the pipes.

A patented modification of this method consists essentially in providing a coating of conducting particles such as coke, for example, embedded in a continuous nonconducting binding material, such as pitch, the theory being that the particles of coke would afford a metallic path for the current through the coating, and thus prevent corrosion of the iron. In practice it has been found that the insulating coating soon breaks down after the manner described above for paint coatings, and when this takes place the particles of coke in contact with the iron set up galvanic action, which causes rapid deterioration of the pipe. It is safe to say that conducting coatings as applied up to the present time have invariably been harmful in their effects because of this tendency to produce a greatly increased amount of self-corrosion.

7. ELECTRIC SCREENS

A method that has been used in some cases to reduce cases of local electrolysis consists in interposing between the pipes and the structure to which it is discharging current a mass of metal which

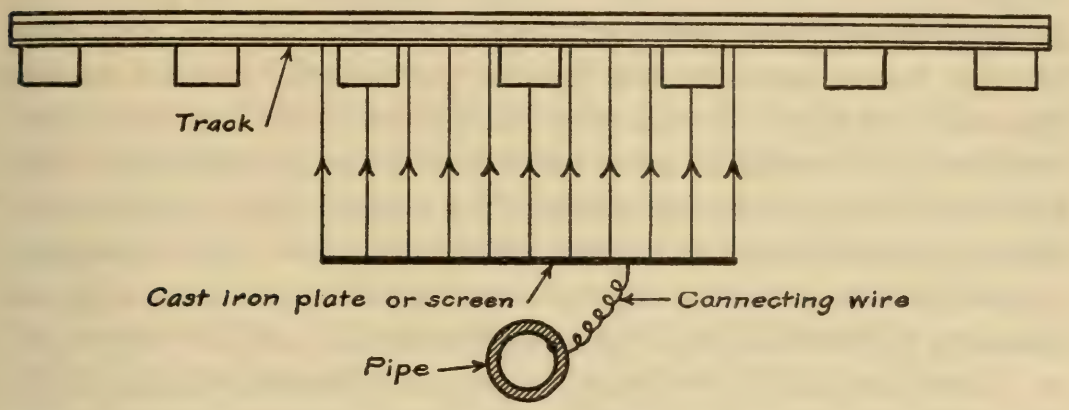


FIG. 9.—*Plane screen*

is electrically connected to the pipe or other structure to be protected. The current is then carried from the pipe to the metal screen by way of the metallic path, and thence discharged into the earth, the corrosion taking place on the screen instead of on the pipe. The screen can be of heavy cast-iron plates or grids. In order to be effective the screen must be placed on the side of the pipe toward which it tends to discharge current, and if the pipe is discharging current in all directions, the screen must take the form of a larger pipe inclosing the pipe which is to be protected.

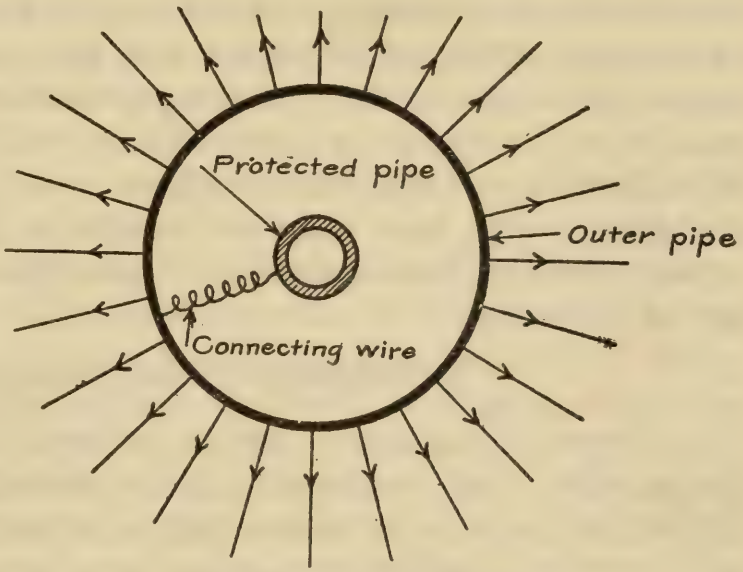


FIG. 10.—*Circular screen*

The principle of such screens is shown in Figs. 9 and 10. Fig. 9 shows diagrammatically a plain screen interposed between the

pipe line and the railway track where the pipe crosses under the track. In this case the tendency would be for the pipe to discharge current upward into the track, so that a small slab of metal, such as cast iron considerably longer than the width of the track and having a width several times the diameter of the pipe interposed between pipe and tracks and connected to the pipe electrically, would take off the greater part of the current on the pipe without injury to the pipe itself; and if the iron slab were very heavy, it would in most cases last almost indefinitely. Fig. 10 shows a circular screen surrounding a pipe which tends to discharge current locally in several directions. The chief advantage of such a screen over a direct bond between the pipe and the structure to which it is discharging current is that the screen has an almost negligible tendency to increase the magnitude of the current flow in the pipes, and therefore can not induce a dangerous condition to the pipes or other structures at remote points, where they are not electrically continuous.

It is obvious that this method is not adapted for extensive use throughout the pipe system, but it may be useful in special cases for relieving severe cases of corrosion in very restricted areas, as, for example, where an important pipe line passes under or very near a street railway line or other pipe system which is strongly negative to the pipe to be protected. At best, however, it should be regarded as a temporary expedient to be resorted to only in emergency, while more adequate mitigative measures are being applied elsewhere in accordance with principles set forth in a later part of this report.

8. INSULATING JOINTS IN PIPES

(*a*) *General Discussion.*—Another method of reducing current flow in pipes which has found rather extensive application within the last few years, in some cases for the primary purpose of reducing electrolysis, but in most cases for other reasons, is that of breaking up the continuity of the pipe lines by the use of insulating or resistance joints, particularly cement joints. In ordinary wrought-iron or steel pipes with screwed or riveted joints the resistance of the joints is usually small in comparison with that of the pipes, and when such pipes are laid in localities where there

is an appreciable potential gradient in the direction of the pipe current of considerable magnitude will usually be carried by the pipe. In the case of cast-iron mains the resistance of the joints is often as great as or greater than a section of the pipe, and it is not uncommon to find a lead joint which has a resistance equivalent to that of several hundred feet or even several thousand feet of pipe, and it is due largely to this high joint resistance and to some extent also to the higher specific resistance of cast iron that cast-iron mains usually carry less current under similar conditions than wrought-iron or steel mains. Experience has shown, however, that the resistance of lead joints is not sufficient to reduce the current to a safe value, and attempts have been made still further to increase the resistance of the pipes by the introduction of specially designed joints of high resistance.

Because of the wide use that is now being made of insulating joints, both for the purpose of protecting against electrolysis and for other reasons, we give below a rather full discussion of the use of such joints and the precautions that should be taken in installing them. It should be emphasized, however, that in general we regard the use of insulating joints as valuable chiefly as an auxiliary measure which may often be used to advantage to supplement measures applied to the railway tracks to reduce voltage drops therein to reasonably low values.

Following the earlier attempts to prevent electrolysis by this method, very strong claims were made for it by some of its advocates, some of them claiming that they had completely solved the problem of electrolysis mitigation by the use of insulating joints. Within a few years, however, a noticeable reaction set in. Many engineers criticized the method, and some of those who were its warmest advocates in the beginning abandoned it. It is but natural, however, that the initial attempts to apply this method should have resulted in some disappointments, and it is not safe to consider these early failures seriously in judging the value of the method when properly applied. At that time no experience had been gained in regard to the frequency with which such joints should be used, the proper location of the joints, the kind of joints best suited to certain conditions, and the complications arising from the presence of other pipe systems not so insulated.

All of these are important factors and must be carefully considered if adequate protection is to be secured.

On account of the very great number of systems, particularly gas systems, which now use cement or other insulating joints, this subject has become a very important one and requires somewhat extended discussion. We therefore give below a rather full statement of the principles underlying the design and construction of the resistance-joint systems where electrolysis mitigation is the primary consideration and also give an account of some of our own investigations that have been completed to date in regard to the use of such joints.

A number of cases have come to our attention where systems in which insulating joints have been installed for the express purpose of preventing electrolysis have, nevertheless, suffered severely from corrosion by stray currents. In every case that we have examined, however, there has been good reason for believing that the trouble was due either to the use of an insufficient number of joints, or joints of improper design, or to the fact that they were not located in such places as to be most effective in reducing danger. A very common procedure has been to insert insulating joints at infrequent intervals of from 200 to 500 feet or to insert a single insulating joint on either side of the track, and a few feet therefrom, and to assume that these insulating joints should prevent current from getting from the railway tracks into the pipes beyond the joint.

The reason why such an installation might fail to protect the pipes in many instances will be evident if we consider the conditions which exist in many places. In the course of voltage surveys in various cities we have often encountered localities where the potential difference over distances of a few hundred feet reach 5 or 6 volts or more during the average all-day load, and considerably higher values during peak load. At times potential gradients of this magnitude have been found to prevail continuously over distances of a thousand feet or more. In a case of this kind, where the difference of potential is, say, 10 volts per thousand feet, and a pipe line is located in a direction approximately parallel to the electromotive force, heavy cur-

rents will, as a rule, be picked up by the pipes, and if this is discharged into the earth, serious damage will, of course, result. If, now, we break up the continuity of the pipe by inserting insulating joints at intervals of, say, 300 feet, these joint resistances, being high compared with the resistance of the pipe, practically all of the potential drop will be concentrated at the joints and across each joint a potential drop of about 3.3 volts will occur.

Since, as usually made, the leakage path around such joints is very short, the metal parts on opposite sides of the joint being brought within an inch or less of each other, it is evident that the potential gradient across this short distance will be extremely high, and as a consequence heavy leakage currents will flow around the joints sufficient to destroy them within a comparatively short time. It is evident that in order to prevent this a sufficient number of insulating joints must be used so that the drop of potential across each joint will not be sufficient to injure the joint within a long period of years. In other words, the total resistance of the line must be so much increased by the addition of the joints that the current flowing through it under the total potential difference will be too small to do serious damage. This points to the importance of governing the number and location of the joints by the local potential conditions, a subject which is taken up in detail in a later part of this paper.

(*b*) *Tests on Insulating Joints in Service.*—In attempting to determine by actual experiment under practical conditions just how effective insulating joints may be in reducing currents in pipes, difficulties are met with owing to the complex and uncertain ramification of the pipe networks. In connection with other lines of field work we have made excavations and measured the flow of current in pipe lines provided with insulating joints at more or less frequent intervals, and by comparing these with similar measurements on lines not provided with insulating joints but otherwise similarly situated, an approximate idea has been gained as to the extent to which the currents are reduced by the joints. In making such measurements the method used was the one most commonly employed by engineers for this

purpose, viz, to expose a portion of the pipes between adjacent joints and with a millivoltmeter measure the drop of potential between two points a measured distance apart. The size, type, and class of pipe being known, and the specific resistance being obtained from tables prepared for this purpose, the current in the pipe could be calculated with a sufficient degree of accuracy for work of this kind.

Wherever practicable the current measurements were made in cities where one pipe system only (either water or gas) was provided with insulating joints, and by selecting places where the pipes of the two systems lay parallel and near together for some distance it was possible to obtain points at which the two systems were subjected to somewhat similar conditions except for the insulating joints, and in this way a fairly definite idea of the effect of insulating joints could be obtained. Such readings are of course not altogether satisfactory, for there was often a difference in the material of the pipe and in some cases a difference in size also, and allowance should be made for these. There was also the uncertainty in regard to the ramifications of the network to which the lines were connected, but in general the conditions were sufficiently similar to indicate clearly the tendency of the joints.

A number of these current readings in parallel mains is shown in Table 3. In test No. 1, the measurements were taken on an 8-inch water main provided with very infrequent leadite joints, and on the same street measurements were taken on a 6-inch gas main provided with lead joints throughout. As shown in the table, the current in the former was 0.93 ampere and in the latter 1.57 amperes, showing an appreciable reduction, although the difference is small. It is important to note, however, that in this case the leadite joints were at a considerable distance apart, averaging several thousand feet, and further, they were not installed with the idea of making them insulating, so that in many cases the joints were of low resistance owing to contact between the bell and spigot ends of the pipes. In test No. 2 measurements were taken on a 12-inch main provided with a leadite joint every 12 feet and on a parallel 16-inch main with lead joints throughout. The difference here is very marked, the current in the lead joint line being over one hundred times that in the line

having leadite in every joint. Similarly, in test No. 3, where also one line was provided with a leadite joint every 12 feet, the difference is more marked, the current in the case of lead joints being about a hundred and twenty times that in the pipes having leadite joints. In test No. 4 the difference is much less, but this is partly due, no doubt, to the difference in size of the pipes, as shown by the table. The chief factor, however, is the distance between the leadite joints, this being in the present instance about 300 feet.

TABLE 3

Effect of Insulating Joints on Current Flow in Parallel Mains

Test No.	Mains			Type of joint	Distribution of insulating joints in mains	Section in which drop was measured		Average potential across section	Amperes in pipe
	Kind	Class	Size			Distance to joint	Length		
			Inches				Feet	Millivolts	
1	Cast	D	8	Leadite	Isolated	Adjacent	9	0.2	0.93
	Do	A	6	Lead	None		6	.4	1.51
2	Do	A	12	Leadite	12 feet	do	11½	.013	.062
	Do	C	16	Lead	None		3	.2	7.27
3	Do	D	12	Leadite	12 feet	do	10½	.013	.094
	Do	C	16	Lead	None		8	.83	11.31
4	Do	D	12	Leadite	300 feet	do	11	.02	.138
	Do	C	4	Lead	None		6	.3	.86
5	Wrought	Standard.	6	No. 6 D.	Isolated	do	3	.005	.037
	Cast	C	6	Lead	None		3½	.8	6.13
6	Wrought	Standard.	4	No. 6 D.	Irregular	do	2¼	.01	.062
	Cast	C	4	Lead	None		10¾	8.0	12.85
7	Wrought	Standard.	6	No. 6 D.	Irregular	do	3	.0025	.0185
	Cast	C	20	Lead	None		10½	1.9	28.22
8	Wrought	Standard.	4	No. 6 D.	Irregular	do	2½	.01	.056
	Cast	C	4	Lead	None		7	.15	.371
9	Wrought	Standard.	6	No. 6 D.	Irregular	do	1⅓	.0025	.042
	Cast	C	6	Lead	None		11⅙	.02	.048
10	Wrought	Standard.	8	No. 6 D.	Irregular	do	2½	.0025	.031
	Cast	C	6	Lead	None		11¾	2.4	5.47
11	Wrought	Standard.	3	No. 39 D.	20 feet	do	22	.005	.0024
	Cast	C	6	Lead	None		10½	2.0	5.11
12	Wrought	Standard.	3	No. 6 D.	Irregular	1000 feet	10	1.2	1.26
	Cast	C	10	Lead	None		10	.3	1.62
13	Wrought	Standard.	3	No. 6 D.	Irregular	1300 feet	4	.01	.026
	Cast	C	12	Lead	None		10	.5	3.50
	do	C	12	do	do		10	.2	1.40
14	Wrought	Standard.	3	No. 6 D.	Irregular	500 feet	10	.015	.016
	Cast	C	10	Lead	None		10	5.0	27.0

TABLE 4

Small Currents Flowing in Mains Protected by Insulating Joints

Mains			Joints		Distribution of insulating joints in mains	Section in which drop was measured		Average potential across section	Amperes in pipe
Kind	Class	Size	Type	Age		Distance from insulating joints	Length		
		Inches		Years			Feet	Millivolts	
Cast	D	12	Leadite	3	12 feet	Adjacent	12	0.013	0.082
Do	D	12	do	3	do	do	10½	.013	.094
Do	D	12	do	3	do	do	11	.013	.090
Do	D	12	do	2	do	do	8	.01	.095
Do	D	12	do	2	do	do	11	.041	.283
Do	D	12	do	3	do	do	11	.01	.069
Do	D	12	do	4	Isolated	do	10¼	.02	.148
Do	D	12	do	4	300 feet	do	11	.02	.138
Do	D	12	Wood	3	Isolated	do	6	.01	.127
Do	D	12	do	3	do	100 feet	6	.03	.38
Wrought	Standard	4	No. 6 D	4	20 feet	Adjacent	8	.0025	.0044
Do	do	6	do	4	Isolated	do	3	.005	.037
Do	do	4	do	4	Irregular	do	225	.01	.00063
Do	od	6	do	4	do	do	3	.0025	.0185
Do	do	4	do	4	do	do	2½	.01	.056
Do	do	6	do	4	do	do	1½	.0025	.043
Do	do	8	do	4	do	do	2½	.0025	.031
Do	do	3	No. 39 D	4	20 feet	do	2⅛	.005	.024
Do	do	3	No. 6 D	2	Irregular	1000 feet	10	.0025	.0026
Do	do	3	do	2	do	1300 feet	4	— .01	— .0263
Do	do	4	do	2	do	200 feet	10	.015	.0211
Do	do	4	do	2	do	Adjacent	3	.025	.1175
Do	do	4	do	2	do	1200 feet	6	.02	.047
Do	do	4	do	2	do	600 feet	6	.01	.0235
Do	do	4	do	2	do	Adjacent	4	.0025	.0088
Cast	C	6	do	2	do	do	3½	.01	.0765
Wrought	Standard	3	do	2	do	500 feet	10	.015	.0157
Cast	C	8	do	2	do	2500 feet	6	.2	1.30
Wrought	Standard	4	do	2	do	750 feet	6	.1	.235
Cast	C	6	Cement	10	12 feet	Adjacent	11	.0025	.0061
Do	C	6	do	10	do	do	11	.015	.0365
Do	C	6	do	10	do	do	11	.05	.122

Tests No. 5 to 11, inclusive, were made on wrought-iron gas mains provided with Dresser couplings at irregular intervals and on parallel cast-iron water mains provided with lead joints. In comparing these figures it should be borne in mind that cast iron has a much higher resistance than wrought iron, and further that the lead joints themselves introduce considerable resistance into the

circuit, so that the real effect of the Dresser joints is much greater than the figures would indicate. While considerable variation exists in the ratios of current in parallel mains in the different tests of this series, they show without exception considerable reduction in current due to the insulating joints. Taking the average of the series we find that the current in the lines having lead joints is about thirty-six times that in the lines having insulating joints.

TABLE 5

Current Mains in Mains When Joints are Infrequent

Mains			Joints		Distribution of insulating joints in mains	Section in which drop was measured		Average potential across section	Amperes in pipe
Kind	Class	Size	Type	Age		Distance from insulating joints	Length		
		Inches		Years			Feet	Millivolts	
Cast.....	D.....	8	Leadite	4	Isolated..	Adjacent.	9	0.2	0.926
Do....	C.....	30	...do...	3	.....d....	.....do....	11	.2	5.45
Wrought.	Standard.	6	No. 6 D	4	Irregular	1000 feet..	3	.04	.296
Do....	...do.....	6	...do...	4	.....do...	600 feet...	2¾	.25	2.02
Do....	...do.....	4	...do...	4	.....do...	300 feet...	2	.11	.775
Do....	...do.....	4	...do...	2	.....do...	200 feet...	19	1.0	.742
Do....	Casing...	5⅝	...do...	2	.....do...	2500 feet..	6	.05	.78
Do....	Standard.	6	...do...	2	.....do...	1200 feet..	2	.4	4.44
Do....	...do.....	8	...do...	2	.....do...	300 feet...	3	.6	6.18
Do....	...do.....	4	...do...	2	.....do...	1200 feet..	2½	.4	2.25

In all of these cases, except in test No. 11, the insulating joints were irregularly spaced, the distance between joints in various parts of the system varying from three hundred to several thousand feet. This fact being considered, the relatively low values of current in the lines provided with insulating joints is quite remarkable. In the last two tests shown in Table 3 (Nos. 13 and 14) the ratios of current in the lead jointed lines to that in the lines with insulating joints are, respectively, 134 and 168, but in these tests considerable allowance must be made for the relatively large size of the cast-iron mains as shown by the table.

In Table 4 is shown a series of current measurements on lines having insulating joints under conditions where, in most cases, it was not possible to obtain similar readings on lines not so insulated, and they are presented here merely to show that in general

these currents have been found to be very low. These figures may be regarded as typical of what may be expected under ordinary conditions where a considerable number of insulating joints are used. That the current in these systems was not invariably small, however, is shown in Table 5, which gives a number of tests showing current of considerable magnitude flowing in the pipes. It is to be noted, however, that in all such cases the insulating joints were widely separated, as shown by the column giving the distance from the nearest insulating joint to the point at which the measurements were taken. The distance between joints being at least double these values, they range, therefore, from four hundred to several thousand feet. These figures emphasize the fact pointed out above that if the joints are placed too far apart in places where potential gradients in the earth are high, enough current may continue to flow through the pipes to cause serious damage.

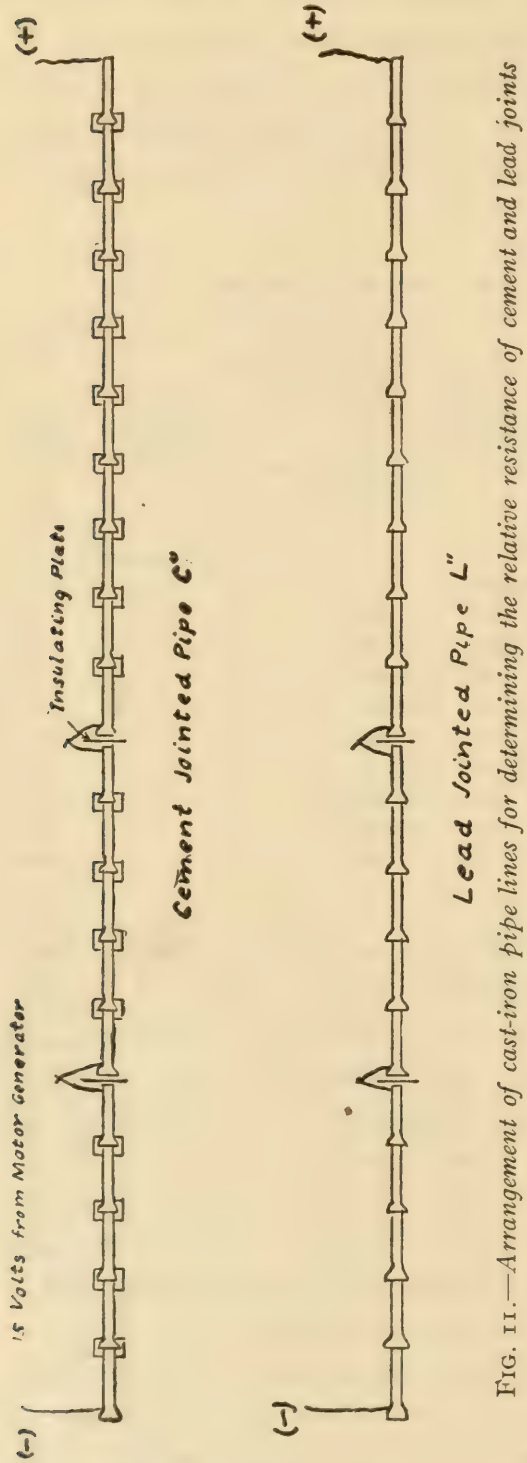


FIG. 11.—*Arrangement of cast-iron pipe lines for determining the relative resistance of cement and lead joints*

In all of the cases above referred to the resistance joints were either spaced at considerable distances apart or were not carefully enough made to insure a high resistance; they do not therefore show what may be accomplished by the use of insulating joints when installed at very frequent intervals and when proper care is taken to eliminate defects in the joints. In order to secure

further and more exact data on this point two experimental lines of 4-inch cast-iron pipe were laid at the Bureau of Standards under conditions which insured identical conditions except for the joints. The lines were laid parallel, 100 feet long and 40 feet apart, one line being provided with ordinary lead joints and the other with carefully made cement joints.

The arrangements of these pipes is shown in Fig. 11. At the center of each line the pipes were separated by a large insulating plate and to the ends of the pipes adjoining this plate insulated leads were attached, and these were brought to the surface and short-circuited, an ammeter being inserted in these leads when it was desired to measure the current in the pipes. A difference of potential of 15 volts was impressed on the pipes and measurements of the current flowing in the pipes were made. The results are given in Table 6, and are a most striking illustration of the effect of carefully installed insulating joints in keeping the currents off the pipes. It will be seen that the current flowing in the line provided with cement joints was, when last measured, less than one twenty-two thousandth part of that flowing in the line having lead joints, and is decreasing. This current is so small as to be entirely negligible, in so far as electrolysis effects are concerned.

TABLE 6

Current in Parallel Cement and Lead Joints

Date	Voltage	Current		Ratio, lead to cement
		Cement	Lead	
May 8, 1911	15	0.0032	29.1	9 100
Nov. 2, 1911	15	.0011	24.2	22 000

It is very important to note that in the systems mentioned above not only have the currents in the pipes been reduced to relatively small values by means of insulating joints, but the systems thus protected have been singularly free from electrolysis troubles since the joints were installed. Although they have been in service for periods varying from 2 to 10 years or longer no serious cases of trouble have arisen, although in some instances other systems laid in the same streets and not so protected have suffered considerable

damage from electrolysis. As an example, we may cite the experience of the Cambridge Gas Co., of Cambridge, Mass. This company uses cement joints exclusively in their gas mains and they have had but little trouble from electrolysis, while the water pipes occupying the same region and not so protected are reported to have suffered severely for years.

(*c*) *Resistance of Various Types of Insulating Joints in Practice.*—While the foregoing shows that insulating or resistance joints when properly installed and used in sufficient number will very greatly reduce the flow of current in pipes, there are certain features in connection with such installations, which, if not guarded against, may give rise to considerable trouble. In the first place, joints designed and installed as insulating joints may or may not be insulating when completed, and this is especially apt to be true after the joints have been in service for a considerable length of time. A little carelessness in making the joint may permit the two ends of the pipe to make metallic contact, in which case, of course, the joint becomes worthless as a protection against electrolysis. This is particularly apt to occur in making joints where cement or leadite is substituted for lead, but it can easily be guarded against with a little care. But even when every care is exercised in making the joints, they will often show surprisingly low resistances after having been in service for a considerable time.

Table 7 shows the resistances of a number of so-called insulating joints in actual service selected at random, and these are typical of what may be expected. In measuring these resistances, a joint and a portion of the pipe were uncovered and the drop across the joint compared with that across a measured length of pipe either by means of a voltmeter or with a slide wire bridge. The size, weight, and material of the pipe being known, the resistance of both pipe and joint in ohms could also be calculated with a fair degree of accuracy. It is to be noted that a number of joints show an extremely low resistance, comparable with that of an ordinary lead joint, thereby indicating metallic contact of the pipes. This is particularly true of some of the leadite joints. It is important to note that the leadite joints were made without any attempt to make them insulating and this may be largely responsible for the large proportion of very low resistance joints.

TABLE 7

Resistance of Joints in Service

Mains			Joints		Average potential across joint	Resistance of joints	
Kind	Class	Size	Type	Age		Ohms	Length of pipe with same resistance
		Inches		Years	Millivolts		Feet
Cast	D	8	Leadite	4	0.8	0.00133	36
Do	D	8	do	4	20.0	.033	897
Do	D	12	do	3	8.0	.123	7230
Da	D	12	do	3	.02	.0003	18
Do	D	12	do	3	.3	.004	235
Do	D	12	do	3	1.0	.014	824
Do	D	12	do	3	5.0	.03	1760
Do	D	12	do	3	5.0	.03	1760
Do	D	12	do	2	.15	.002	118
Do	D	12	do	2	4.0	.018	1060
Do	D	12	do	2	11.0	.051	3000
Do	C	30	do	3	60.0	.015	3350
Do	C	30	do	3	5.0	.0012	269
Do	D	12	do	3	3.0	.0052	306
Do	D	12	do	3	3.0	.0052	306
Do	D	12	do	3	.6	.0113	665
Do	D	12	do	3	.12	.226	13 300
Do	D	12	do	4	40.0	.357	21 000
Do	D	12	do	4	30.0	.268	15 700
Do	D	12	do	4	40.0	.357	21 000
Do	D	12	do	4	3.0	.028	1650
Do	D	12	do	4	6.0	.057	3350
Do	D	12	18-foot wood stave	3	4000.0	40.0	2 350 000
Wrought	Standard	4	No. 6 D	4	57.0	2.64	155 000
Do	do	6	do	4	60.0	.36	37 600
Do	do	4	do	4	1300.0	4.96	292 000
Do	do	6	do	4	400.0	4.65	480 000
Do	do	4	do	4	100.0	.425	25 000
Do	do	6	do	4	800.0	5.35	560 000
Do	do	8	do	4	750.0	9.0	1 400 000
Do	do	4	do	2	400.0	10.65	626 000
Do	do	4	do	2	200.0	9.5	558 000
Cast	C	6	do	2	80.0	.286	60 800
Do	C	6	Cement	10	0.01	.002	42

Perhaps the most surprising feature of Table 7 is the low resistance shown by the Dresser couplings which had been in service for a number of years. Although these joints are provided with rubber gaskets and doubtless had a very high resistance when new, the resistances have now fallen to a few ohms. A joint hav-

ing a resistance of this magnitude, however, is practically as good as one of much higher resistance, since only currents of negligible value can flow through such a resistance under the differences of potential that would commonly prevail across the joint in practice. In the case of the joints having a resistance of a few hundredths of an ohm or lower, currents of considerable magnitude may be found, and these can not be regarded as satisfactory resistance joints. With reasonable care in the making, however, all joints whether made of cement or wood or some special joint provided with rubber or other insulating gasket will have ample resistance, and if properly located and used in a proper manner any of these joints should prove effective.

Leadite joints when new also have ample resistance, comparing favorably with cement joints in this respect, but their resistance appears to decrease rapidly with age. This is very strikingly shown in Table 8, which shows the variation of the resistance of some leadite joints with time. A pipe line about 100 feet long was laid with leadite joints, care being taken to make all joints free from metallic contact between the ends of the pipe. At the center of the line the pipes were separated and an insulating plate inserted, and the two ends of the pipe on either side of the insulating plate were provided with insulated leads, in which an ammeter could be inserted for the purpose of measuring from time to time the current flowing in the pipes. A difference of potential of 15 volts was impressed on this line continuously for several months; this was sufficient to give a drop of potential of about 0.8 volt on each joint.

TABLE 8

Showing Variation of Resistance of Leadite Joints with Time

	July 7, 1911	July 14, 1911	July 21, 1911	July 28, 1911	Aug. 11, 1911	Aug. 25, 1911	Sept. 8, 1911	Sept. 19, 1911	Feb. 19, 1915
Current.....	0.0069	0.0076	0.046	0.268	0.064	0.360	1.24	1.88	132.0
Resistance...	2,174	1,990	326	56	23	41	12	8 ohms	0.113

The readings show that the current was very small when the pipe was first laid, but increased rapidly with time, and after being laid 4 months the resistances had decreased to about one two-thousandths of their initial value and were still decreasing.

At the end of that time the current was discontinued and the pipes were allowed to stand in earth for about 14 months, when the resistance of the line was again measured. It was then found that the resistance of the entire line had fallen to 0.25 ohm, and after about 4 years the resistance was only 0.113 ohm, or less than one nineteen thousandths part of its value at the beginning. This resistance is still high enough to have an appreciable value in reducing current flow in the pipe, the resistance of the joints being still nearly twenty times that of the pipes, but the results indicate that leadite joints can not be depended upon to remain permanently insulating, and their permanent value as a preventive of electrolysis is at least questionable. At first it was supposed that the apparent decrease in the resistance of the joints might be due to increased leakage around the joints, but measurements made of some of the joints when uncovered show that the resistance of the joint itself has decreased. It was found that the leadite contains a large amount of sulphur, and when placed in wet soil this gradually oxidizes forming sulphuric acid which appears to be chiefly responsible for the steady falling off of the resistance of the joints.

(*d*) *Number of Insulating Joints Required.*—A condition already referred to that is likely to cause trouble is a too infrequent use of insulating joints, and this condition is probably responsible for a good deal of the disfavor into which this method has fallen with some people. Obviously, if the joints are placed far apart, the long stretch of intervening pipe may pick up considerable current, and since most of this current must flow out of the pipe as it approaches the insulating joint, serious electrolysis may occur on the positive side of the joint. The more frequently the joints are placed the less the danger from this source. It is of course impossible to lay down any very definite rules in regard to the frequency with which such joints should be used, since that must be determined in each case by local conditions. In general, however, it may be said that the resistance joints should not be confined to the positive area as some have supposed, but should be distributed throughout the negative and neutral areas also. All lines which run near by, or cross under street railway tracks, are generally most in need of resistance joints.

In many cases where there is good reason for believing that the drop of potential is fairly uniformly distributed throughout the entire region in which the insulating joints are to be placed, it is sufficient simply to determine the total difference of potential between the ends of the line affected and use this value in determining the number of insulating joints that are needed in order that the drop of potential across each joint shall not exceed a predetermined value. It usually happens, however, that the potential gradient may vary greatly in different portions of the line and if the joints were uniformly spaced in such cases, the joints would either be more frequent than necessary in some places, or too few in others, and the condition of maximum of protection at a minimum cost would not be realized. This condition is very likely to occur where a pipe line runs at right angles to railway lines, in which case the potential gradient along the pipe will often be many times greater at points within a short distance on either side of the track than at more remote places. Other conditions, such as the presence of other pipe systems, may also disturb the uniformity of the potential drop.

In some instances, as in laying new lines where some cheap type of joint is being used, it may often be less expensive to allow a liberal factor of safety and install enough joints to be safe under any conditions that may arise; but in other cases, as, for instance, where insulating joints are to be inserted in large and important mains already laid, where the cost of each joint is an important matter and where interruption of the service is of serious moment, it is important that no unnecessary joints be used, and that these be so placed that they will be most effective in reducing current flow in the pipes, and so that there will be no danger of developing a high enough difference of potential across the joint to cause trouble. For this reason, before attempting to install a series of insulating joints for the purpose of preventing electrolysis in cases where it is important for economic or other reasons to use as few joints as possible, it is important, first, to make a careful potential survey of the district to be affected and determine the magnitude of the potential gradients in a direction parallel to the pipe lines. This will enable one to determine in advance the approximate number of joints that will be necessary and also the proper loca-

tion of the joints, so that the drop of potential across any joint may not exceed a certain amount.

If a new line is to be laid, it is safe to assume that the average potential gradient after the pipe has been laid will not differ greatly from that which prevails beforehand, provided the joints are used at proper intervals; but the distribution of this potential gradient will be greatly altered, practically all of the fall of potential occurring at the joints. The average drop of potential across joints in any given portion of the line will be approximately equal to the total drop divided by the number of joints. When insulating joints are to be placed in old lines it is well to bear in mind that the insertion of the joints in the pipe will, in general, increase the potential gradient along the pipe due to reduction of current flow in the pipes. This increase may reach as much as 100 per cent or more, and allowance should be made for this.

In actually measuring the potential gradients in the earth special precautions must be taken if trustworthy results are to be obtained. The best procedure to be followed in work of this sort is discussed in detail in Technologic Paper No. 28 of the Bureau of Standards, entitled "Methods of making electrolysis surveys."

After a series of joints are installed the only method of determining experimentally whether or not a sufficient number of joints has been installed is by measuring the drop of potential across each joint and by measuring current flow in the pipes. If the joints are too few in number in any locality, there will be too high a voltage across the joints, and the consequent heavy leakage current may injure the pipe on the positive side of the joint.

As to the voltage that can be safely permitted, that is a matter which depends on a variety of conditions, such as the nature of the soil, kind of joint used, etc., and can only be roughly indicated here. Careful observation of joints under average conditions for a considerable period, together with experiments to be described later, indicate that in cast-iron mains a drop across the joint of from 0.1 to 0.4 volt can usually be regarded as safe, while in wrought-iron pipes a voltage not exceeding about one-third of these values should be allowed. The lower limit applies to pipes located in low, wet places and to joints having a short leakage path between the sections of the pipe, and the upper limit to pipes in

comparatively dry soils and to joints having a long leakage path. This matter of the length of the leakage path around the joint is an important one and is treated later in discussing the relative value of different kinds of joints. If the joints used have not a very high resistance, as when leadite is used, for instance, considerable current may flow through the joints without making a dangerous drop across the joint, and the currents thus collected in a large number of branch lines may ultimately be carried to a few lines in a remote quarter and there give rise to serious damage. In order to guard against this, current measurements in the pipes should also be made. If in any line a considerable current is found to be flowing, or if the voltage across the joints exceeds considerably the limits mentioned above, additional joints should be installed, or measures should be taken to reduce potential drops in the railway return systems. The latter course should be followed where practicable.

One of the problems encountered in attempting to protect a pipe system by the use of resistance joints is the effect of other pipe systems in the same territory not so protected. Gas and water systems, for instance, are often brought into metallic contact with each other in many places, and this greatly increases the difficulty of protecting either system alone by the use of resistance joints. This difficulty could be largely avoided by inserting an insulating joint in the service pipe inside of the buildings in which metallic connections with the other system is made. This would usually be expensive, however, and there are other complications which are not so easily dealt with; where an uninsulated pipe system occupies the same territory with an insulated system, isolated cases of electrolysis are likely to occur.

When a line having insulated joints must be connected to another line not so insulated trouble may be experienced, due to the tendency to develop high potential drops across the joints in such places, particularly if the insulated pipe line is at a potential considerably different from that of the earth, either positive or negative. This condition is especially likely to occur if the uninsulated main is connected to negative return feeders, and those joints near which the negative feeders are attached, are often subjected to unavoidable differences of potential that may be sufficient to

destroy the joint in a short time. For this reason the use of insulating joints and negative return feeders in the same system should be avoided.

The difference of potential that can safely be permitted across a joint presents a problem of great importance and one to which comparatively little study has been given. Some of the factors governing this are mentioned above and one of the most important of these is the type of joint used. It is well recognized that the actual damage due to the discharge of current from a pipe depends not so much on the total quantity of electricity discharged but mainly on the distribution of the discharge. If the current leaves the pipe uniformly over a large surface, a much longer period must elapse before serious damage will result than if the intensity of current discharge is much greater at some points than others, so that conditions which tend to prevent concentration of discharge will correspondingly reduce the danger. As already shown, even pipes provided with insulating joints will carry some current, and especially if the joints are not very frequent; and since with high resistance joints most of this current must leave the pipes at every joint, it becomes important to determine as accurately as possible what the distribution of this discharge may be and to find how this distribution may be made most nearly uniform.

(*e*) *Effect of Form of Joint on Distribution of Leakage.*—To determine the effect of the form of the insulating joint on the distribution of current around the joint, three perfectly insulating joints were made of 4-inch cast-iron pipe, one a bell and spigot joint with a layer of paraffin separating the pipe sections, the second a butt joint with one-half inch of paraffined wood separating the pipes, and the third a similar butt joint with 5 inches of paraffined wood between the pipes.

The pipes in succession were placed coaxially in a cylindrical tank of water 23 inches in diameter and 32 inches in depth with the joint near the center of the tank. The arrangement of the apparatus is shown in Fig. 12. The bottom of the tank was covered with a layer of paraffin and the end of the pipe rested on a glass plate. Rubber-covered leads attached to the pipes 14 inches from the joints permitted the impressing of any desired voltage on the joints.

An L-shaped, two-conductor rubber insulated cable was lowered into the water, the plane of the L being kept radial to the pipe and the end of the L bent upward so that the line joining the exposed ends of the wires at the terminus of the L was normal to the surface of the pipe. Since the specific resistance of the water was substantially uniform throughout, the potential gradient at any point was proportional to the intensity of the current at that

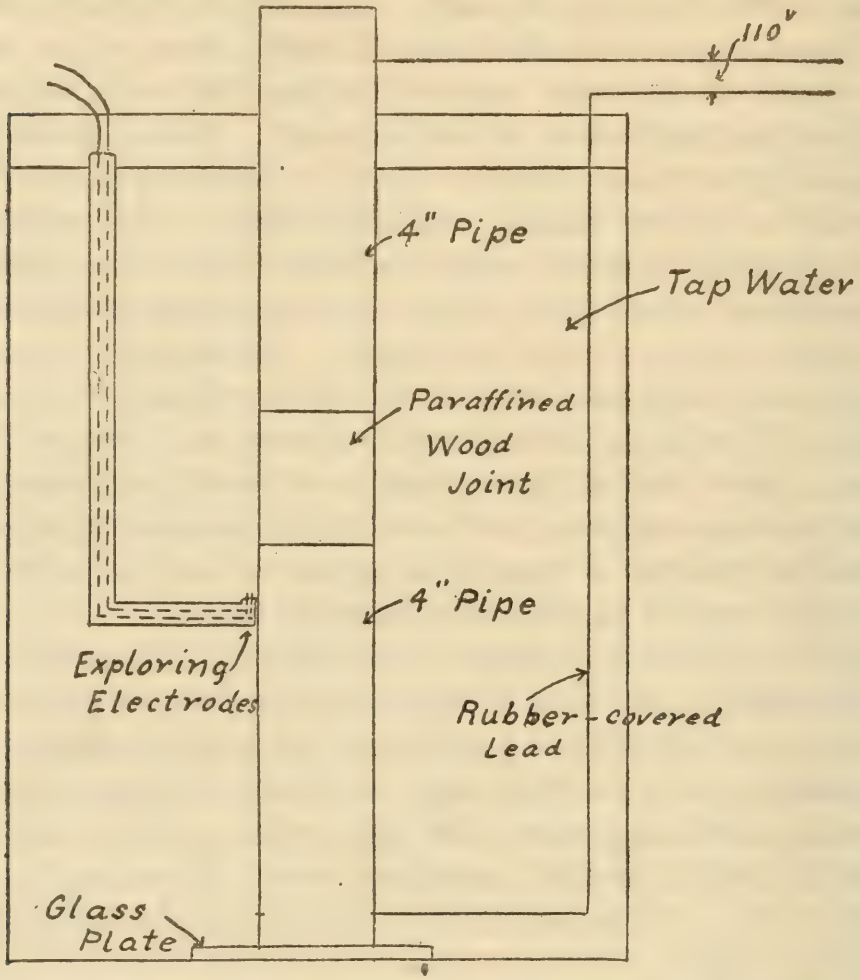


FIG. 12.—*Apparatus for determining the effect of the form of insulating joint on current distribution*

point; hence by measuring the difference of potential between the two exposed ends of the wires when placed as close as practicable to the surface of the pipe (about 0.04 inch), a measure of the current density was obtained. The potential gradients thus obtained at any point divided by the specific resistance of the water gave the intensity of current at that point, and by raising or lowering the L the intensity of current discharge at any desired

point could be found. The specific resistance of the water used was 5620 ohms per centimeter cube which is about the mean of that of a large number of samples of earth taken from a number of cities. It was necessary to impress rather high voltages across the joint and use a voltmeter of high-current sensitivity in order that the pressure readings would not be seriously affected by polarization at the terminals. From 20 to about 100 volts were used, according to the type of joint under test.

The results of the tests are very strikingly shown in the curves of Fig. 13, in which the intensity of current discharge is plotted as a function of the distance along the pipe for some distance on each side of the joint. In each case the axis of the pipe is taken as the zero axis of current and positive values represent flow of current away from the pipe, while negative values represent current returning to the pipe. For convenience in making comparisons all the readings are reduced to values corresponding to a difference of potential of 20 volts across the joint. The curves indicate that the form of the joint has a most decided effect on the distribution of current discharge. The bell and spigot type shows a very high density of current just under the edge of the bell, indicating a very high rate of corrosion at that point. The butt joint, shown at the bottom, having a length of one-half inch, shows a much better distribution of current, the maximum intensity being about one-third that in the case of the bell and spigot joint. With the joint 5 inches long, still further reduction in the height of the peak is shown, the maximum intensity of discharge being only 15 per cent of that of the bell and spigot type.

It is also very interesting to note that the total flow of current about the joint does not differ greatly in the three cases, the resistances of the leakage path being 68, 72, and 87 ohms in the bell and spigot, half-inch and 5-inch joints, respectively. Particularly significant is the comparison of the two butt joints in this respect. Although one is ten times as long as the other the resistance of the leakage path is increased only about 20 per cent. This shows the unwisdom of attempting to reduce the current flow in a pipe line merely by increasing the length of a few joints. The short joints are, as a rule, much cheaper and easier to install and they can therefore be installed much more frequently for the same total cost.

As a rule, therefore, it would appear preferable in installing a line of insulating joints to use a large number of short joints rather than a few long ones, as in this way the current in the pipes can

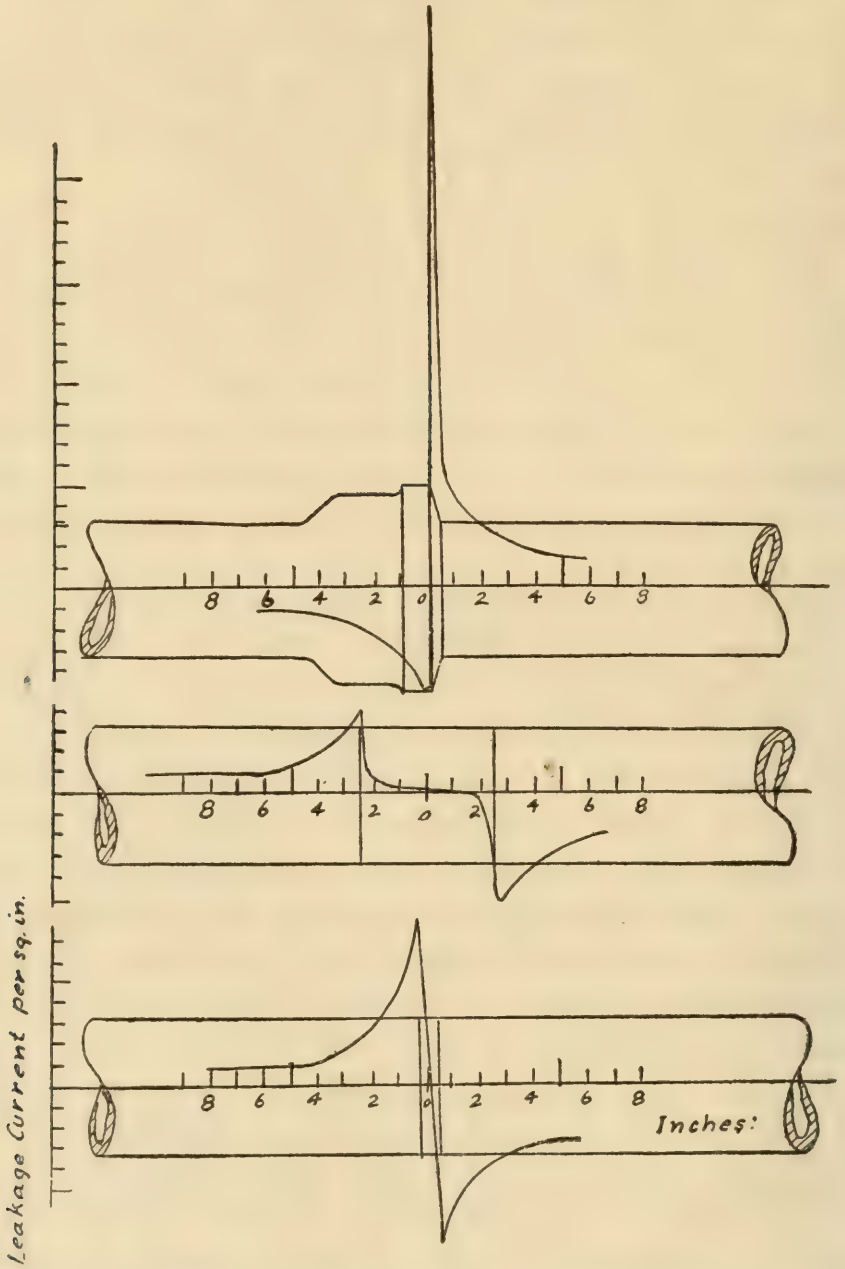


FIG. 13.—*Curves showing intensity of current discharge near insulating joints*

be kept at a much lower volume, and the relatively large number of joints will usually be sufficient to prevent any serious potential drop across the joint. In some cases, however, as where the insu-

lating joints are discontinued, or where for any reason it is necessary to use but a few joints or to put them in places where high potential differences are unavoidable, the above tests show that the long joint is much to be preferred, because of its effect in preventing great concentration of current discharge near the edge of the joint.

Owing to the possibility that polarization effects or contact resistance between soil and pipe might seriously affect the distribution of current flow, the following experiment was carried out with a view of checking the accuracy of the deductions made from the current distribution curves of Fig. 13. For this purpose an apparatus was made up like that shown in Fig. 14. This consisted of an insulating joint *A*, made of paraffined wood, on one

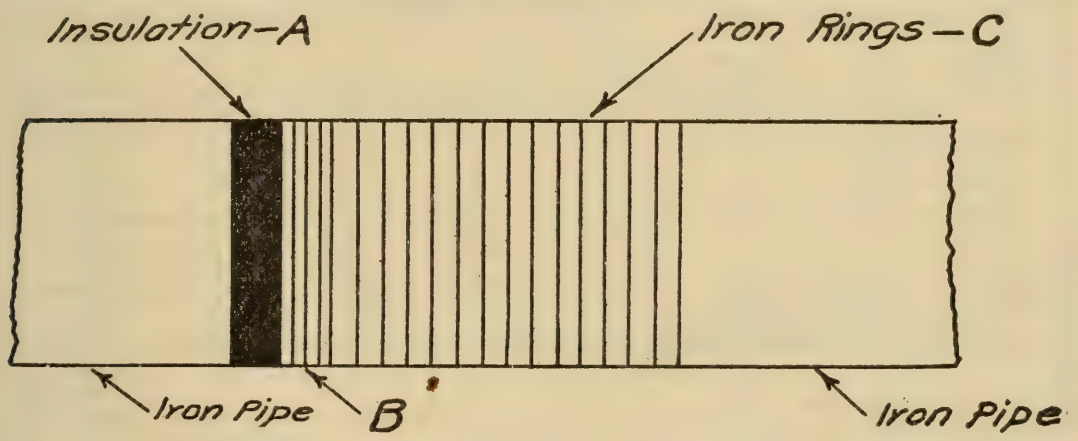


FIG. 14.—*Insulating joint for determining distribution of corrosion in earth*

side of which was a short section of ordinary wrought-iron pipe *B*, and on the other side was a series of thin circular disks *C*, placed as shown in the figure. These disks were all electrically connected together, so that they were at the same potential. The object was to bury the joint in earth and impress on it a moderate potential difference with the thin circular disk on the positive side and determine the relative amount of corrosion on the different disks as a function of their distance from the insulating joints in order to see how this compared with the potential distribution curve around the joint as shown in Fig. 13. Before assembling, the individual disks were carefully cleaned and weighed. The joint was then buried in the earth and a potential difference of 15 volts impressed on it for a period of several months with the cir-

cular disks on the positive side; it was then removed, the disks taken apart, carefully cleaned and weighed, as before, and the loss determined.

The result of the test is shown in Fig. 15, in which the curve represents the loss in weight of the disks as a function of the distance from the insulating joint. By comparing the shape of this curve with the current distribution curves of Fig. 13 it will be seen that they have substantially the same form, which shows that the method used in determining the curves in Fig. 13 gives a

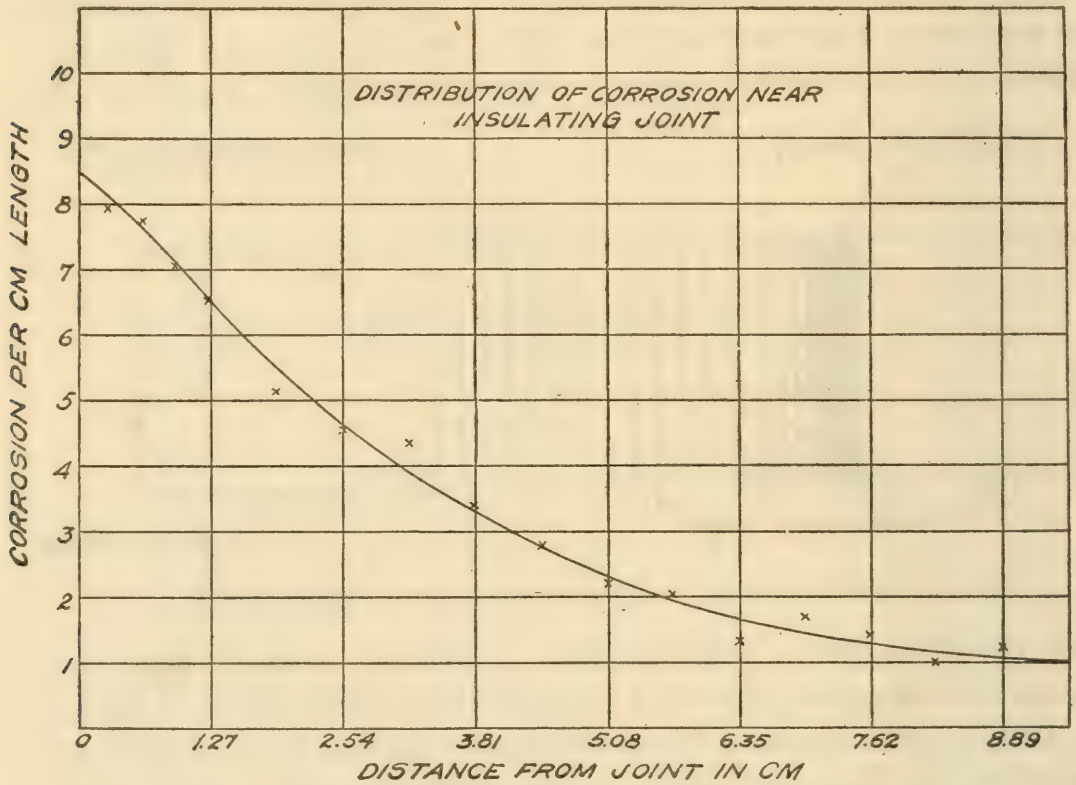


FIG. 15.—*Distribution of corrosion near insulating joint*

current distribution which is substantially the same as that which actually occurred in the case of the insulating joint buried in soil.

(*f*) *Limiting Safe Potential Drops on Insulating Joints.*—The above results furnish also a basis upon which can be made a roughly approximate determination of the voltage drop which may be permitted across a joint of the type tested. It can be shown that the rate at which corrosion will penetrate the iron is given by the formula $L = \frac{C}{D} \times \frac{P}{S}$, where L is the rate at which the

corrosion penetrates the iron expressed in centimeters per year, C is the electrochemical equivalent of iron, D its density, P the average potential gradient in volts per centimeter normal to the pipe at the point considered, and S is the specific resistance of the soil in ohms per centimeter cube. The assumption is here made that the coefficient of corrosion is 100 per cent. For cast iron the value of $\frac{C}{D}$ is about 1280, and the equation becomes

$$L = 1280 \cdot \frac{P}{S}$$

Assuming 5600 ohms per centimeter cube as the average specific resistance of the soil and a drop of potential of 0.4 volt across the joint and determining from the curves in Fig. 13 the maximum current intensity reduced to this voltage, we get as the maximum rate of penetration of the corrosion in inches per year:

	Inches per year
Bell and spigot joint	0.034
One-half inch wood joint	.009
Five-inch wood joint	.004

The time required for the corrosion to penetrate clear through a pipe one-half inch thick containing these joints is therefore as follows:

	Years
Bell and spigot	14.7
One-half inch wood	53.4
Five-inch wood	121

The permissible drop across a joint in one-half inch cast-iron pipe for a life of 40 years is as follows:

	Volts
Bell and spigot joint	0.147
One-half inch wood	.53
Five-inch wood	1.22

In considering these figures it is well to remember that the corrosion here indicated is that due to electrolysis and is in addition to the self-corrosion that may also occur. It should be added that we have found the specific resistance of soils to be in some cases as low as one-tenth of the value used in these calculations, so that under practical conditions the rate of corrosion may be several times that computed above. Further, the effect of surface resistance due to paints, etc., and the effects of polarization under

low voltages are not here considered, so that considerable variations from the calculated values may be expected. These calculations are of value only in that they indicate that a drop of potential across a short joint can hardly be considered safe if it exceeds a few tenths of a volt even under the best conditions, and that much can be gained by the use of a long leakage path where the voltage at each joint is necessarily high. This problem is an important one and much additional work remains to be done in this direction.

(*g*) *Types of Insulating Joints Available.*—It is well to call attention at this point to some of the various types of insulating joints that are now in use. These may be divided into four classes, viz:

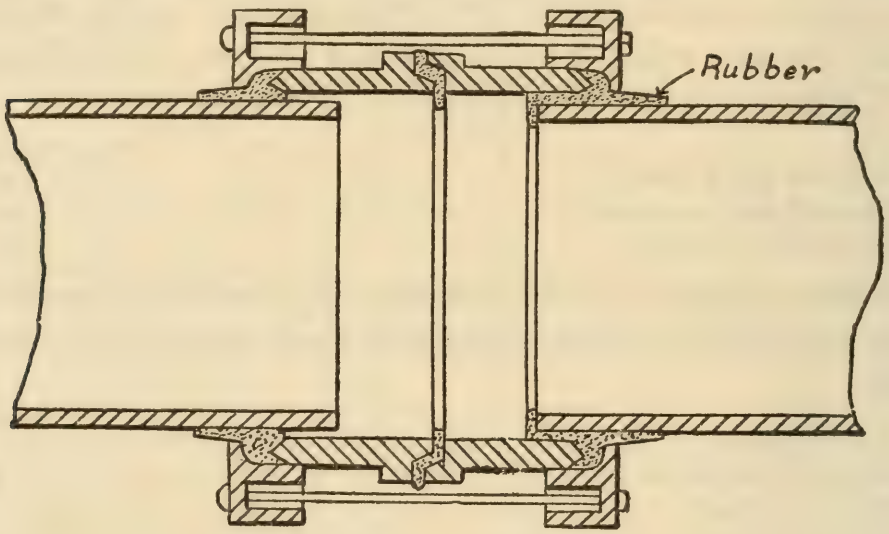


FIG. 16.—*Dresser coupling*

(1) Clamped joints, using a rubber gasket or other insulating material to make a tight joint and provide the insulating section; (2) wooden joints, including wood-stave pipe sections; (3) cement joints, of which there are various types; and (4) leadite joints.

The first of these, exemplified by the well-known Dresser coupling, is quite extensively used for the purpose of securing gas-tight joints, and some types of these are designed also to give insulating joints. When properly designed and installed, it gives a very high-resistance joint, and has been very effectively used in a number of instances for the purpose of reducing the flow of current in the pipes. The construction of one form of Dresser coupling, known as the divided center ring insulating coupling,

is shown in Fig. 16. This makes a very satisfactory insulating joint for most purposes, although it may, under bad voltage conditions, be liable to injury because of the relatively short leakage path, the importance of which has already been discussed. Under most circumstances, where the local potential gradients are not too high, this should cause no trouble. Some trouble has been reported where these couplings have been used on artificial gas mains, owing to the deleterious effect of the gas on the rubber gaskets. They do not appear to be affected by natural gas, however, and in such mains they appear to show a satisfactory life.

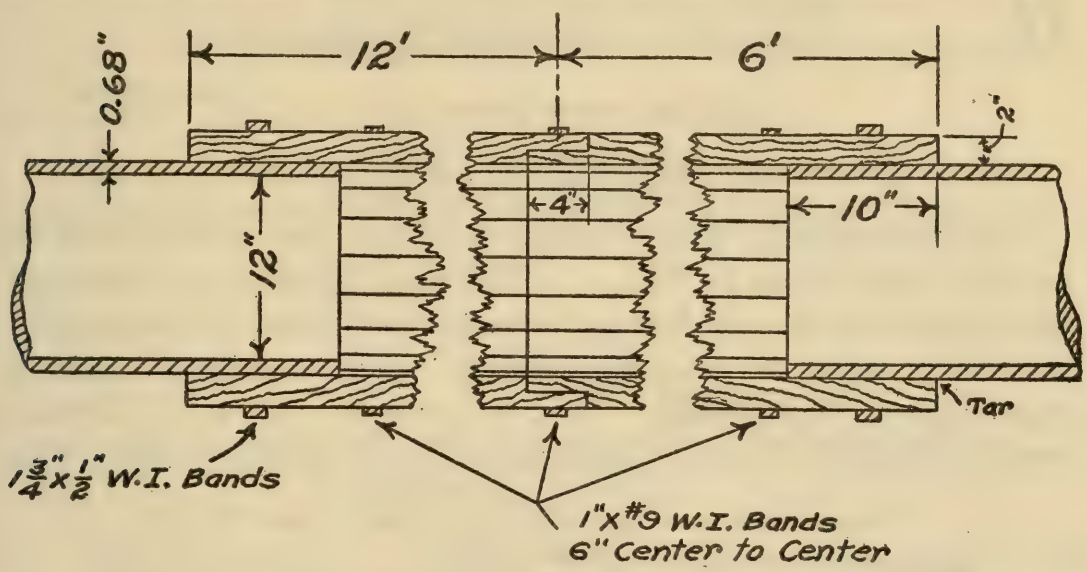


FIG. 17.—*Wood stave joint used by the Pennsylvania Water Co.*

Of the wooden joints, numerous modifications are in use. One type used by the Pennsylvania Water Co. is shown in Fig. 17, which is self-explanatory. This joint has a high electrical resistance and is particularly adapted for use in places where only one or at most a few joints are installed and the drop of potential across the joint is likely to be high. The great length of the joint is very effective in causing any leakage current around the joint to distribute itself over a considerable length of adjoining pipe, as pointed out above, and thus prevents concentration of electrolysis at the edge of the joint.

Another type of wood-stave joint is shown in Fig. 18. The spiral steel band used in this construction would have the effect of materially shortening the leakage path, and while it would have

ample resistance to serve as an insulating joint under most circumstances, it could not safely withstand as high a drop of potential across the joint as the one previously described.

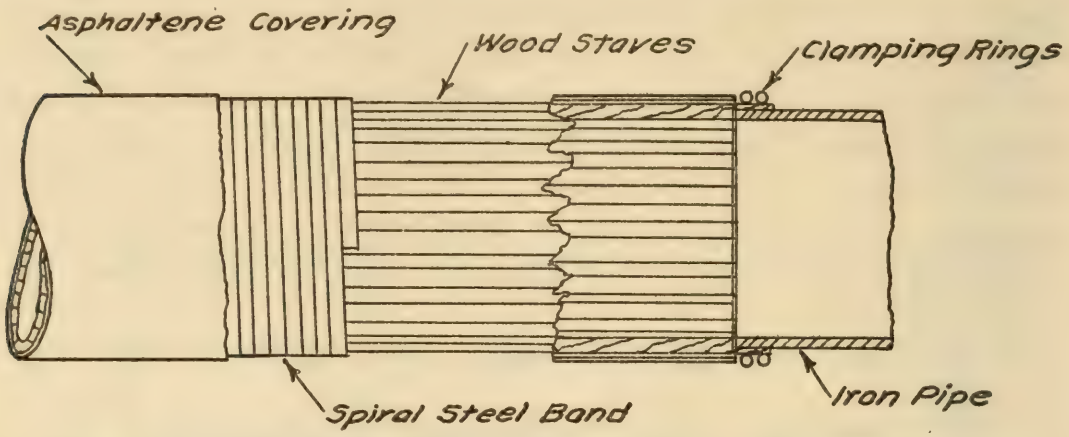


FIG. 18.—*Construction of Wyckoff stave pipe, showing connection to iron pipe*

The Metropolitan Water Board of Boston has used a type of wooden joint shown in Fig. 19. This joint is simple in construction, consisting of a one-half inch wooden liner made of overlapping sections of wood, the ring thus formed being wound with canvas impregnated with paraffin. The purpose of this is to prevent possible metallic contact between the ends of the pipes. The

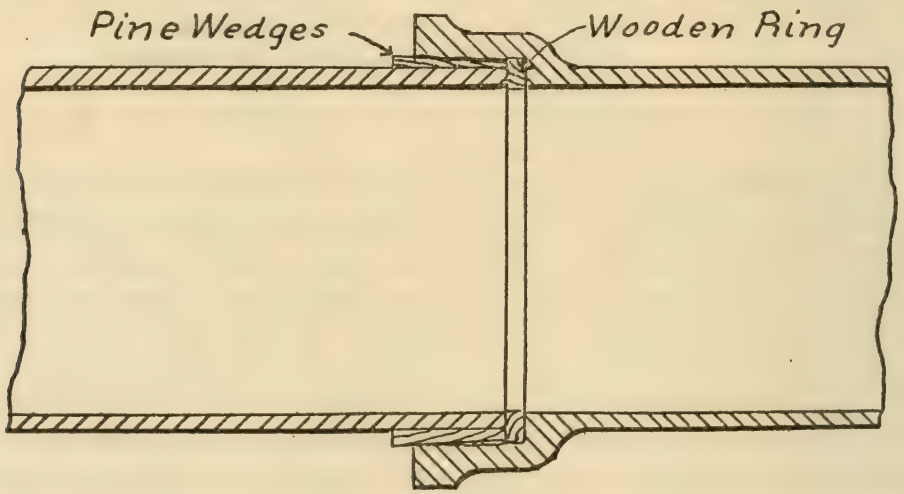


FIG. 19.—*Type of insulating joint used by Metropolitan Water Board of Boston.*

wooden staves are of clear white pine, planed to fit the curvature of the pipe, and are driven in by a special driver to prevent splintering. Any leaks that may develop are stopped with white-pine

wedges. These joints have been found to be very satisfactory up to about 75 pounds pressure. Higher pressures sometimes cause moderate leakage through pores of the wood, and this has been overcome by dipping the inner ends of the staves in red lead. In some cases the staves are reinforced by an iron band clamped around the spigot end of the pipe. Usually a slight change is made in the castings where this joint is to be inserted, the spigot end being cast without bead and the inside of the bell smooth without groove.

The cost of these joints has been given as ranging from $5 to $12 when installed in new lines, but when installed in old mains the cost would be much higher. The resistance of this joint is

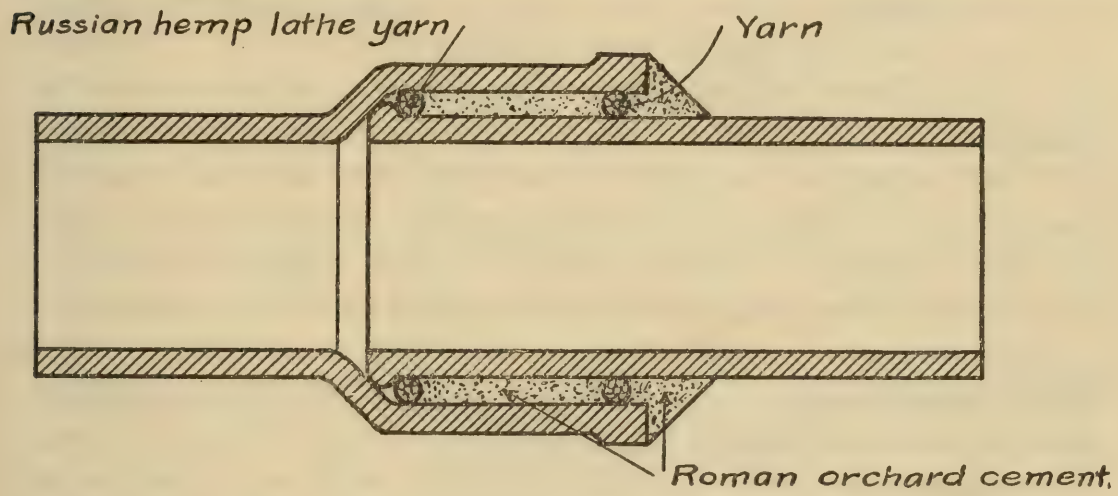


FIG. 20.—*Cement joint used by Cambridge Gas Light Co.*

ample under all circumstances that may arise, but the relatively short leakage path would often make it necessary to use the joint with greater frequency than would be necessary with joints having a long leakage path.

Cement joints have been given a variety of forms, and one which has been used successfully for years by the Cambridge Gas Light Co. is shown in Fig. 20. In making this joint the inner ring of hemp is chosen exactly the right size to fill the annular space between bell and spigot, and this is rolled in when the pipes are set together and driven hard with the calking tool. As usually made by the Cambridge company no special attempt is made to keep the metal of the two adjacent lengths of pipe apart; not-

withstanding this fact, the resistance of the joints has, on the whole, been high enough to prevent the accumulation of any considerable amounts of stray currents, and as a consequence this system has never been troubled by electrolysis, although the pipes of the Cambridge Water Co. are said to have suffered severely.

After thoroughly tamping the ring of hemp into place the cement is carefully worked into the joint with trowel and calking tool until the space between bell and spigot is filled flush with the face of the bell. Another turn of hemp the same as the first is then laid against the cement and driven in with the calking tool just under the edge of the bell. The cement is in this way rendered very compact, and it is claimed that on this feature depends in large measure success of the joint. A collar of cement is finally laid over the outer ring of hemp to protect it from rot. If success is to be achieved with this joint, great care must be exercised in the making of the joints. Perfect cleanliness of the inside of the bell and outside of the spigot is necessary, and all loose scale and sand should be removed before the cement is put in place. Only the best quality of cement should be used and this should be thoroughly mixed and tamped into the joint with the greatest care.

In some cases careful bedding of the pipes is important, as the cement joint is much less yielding than lead, and if any considerable lateral movement of the pipes takes place it is liable to break the pipe, the strength of a well-made joint being as a rule greater than that of the pipe itself. In some instances, instead of making every joint of cement, every third or fourth joint only is made of cement, the others being lead. Except in extreme cases this seems likely to prove practically as effective in minimizing electrolysis troubles, and it has the great advantage that the lead joints impart a flexibility to the system that will greatly reduce troubles due to lateral motion of the pipes.

The principal defect of the joint just described from the point of view of protection against electrolysis lies in the fact that no provision is made for preventing metallic contact between the bell and spigot end of the pipe. In order to guard against this a modified construction, shown in Fig. 21, can be used. This is the same as Fig. 20 except that an insulating ring *A* of rubber or fiber or other suitable material is inserted to prevent actual metallic contact

between the ends of the pipe. Such a joint should answer all requirements for ordinary service where joints are used at very frequent intervals, so that the drop of potential across the joint is not great enough to require a long leakage path.

The use of leadite for joints has been confined chiefly to water mains, and for such service some prefer it to any other material, although it has not always met with favor. This material is melted and run into the joint after the manner of a poured-lead joint. It is cheaper than lead and some claim that it makes a better joint mechanically, but many dissent from this view. It often happens that when the joints are first made a large proportion of them will show considerable leakage, but in the presence

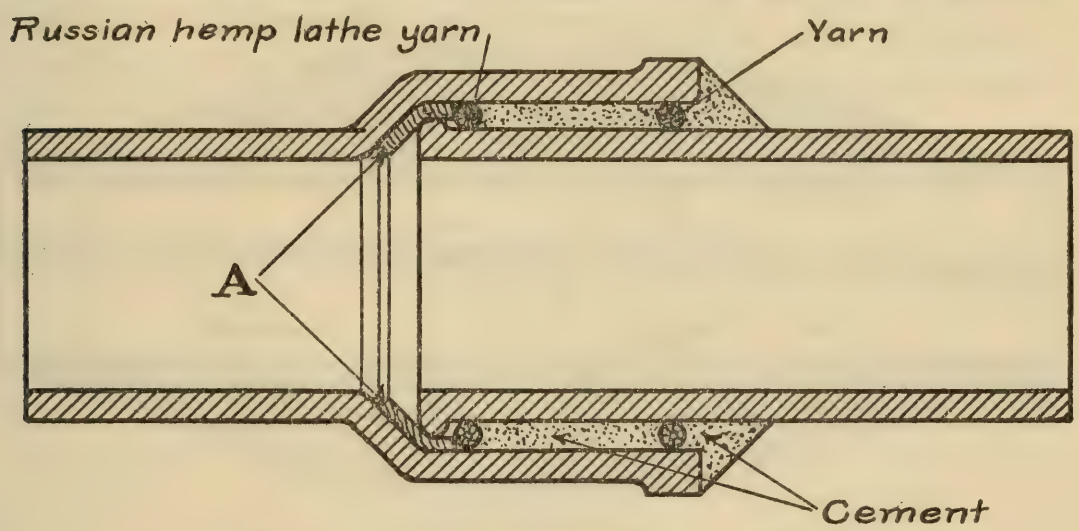


FIG. 21.—*Cement joint*

of water they seem to have a tendency to seal themselves up and the leaks will usually cease entirely within a day or two.

It is very important to see that a dense mass completely fills the joint, and it is lack of care in this respect that is probably responsible for most of the trouble with leaky joints. The runner used in pouring the joint should be so designed that there will be a head of 8 to 10 inches above the joint. If the material is at proper temperature this head is usually sufficient to insure a dense homogeneous mass of leadite in the joint. As already noted, the resistance of leadite is very high when first run, but after lying in the ground for some time its resistance decreases greatly, and until further experience has been had we would not recommend

them unreservedly as suitable for preventing electrolysis, although they may be found valuable for this purpose.

(*h*) *Increasing the Length of Leakage Path Around Joint.*—Inasmuch as short insulating joints are much easier and cheaper to build than long joints, it is well to discuss here some possible means whereby a long leakage path may be given to a short insulating joint and thus combine in one joint a certain measure of the economy and ease of construction of the short joint and the greater protective tendency of the long joint. A joint embodying these features is shown diagrammatically in Fig. 22. In this case the insulating joint proper between the bell and spigot is made with cement in the usual way, care being taken to prevent metallic

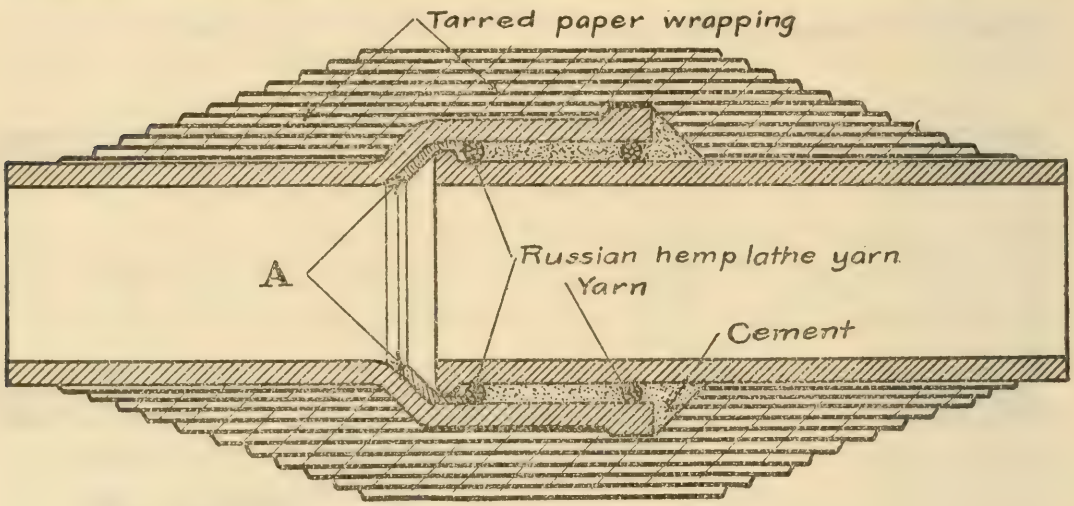


FIG. 22.—*Cement joint with long leakage path*

contact between the ends of the pipes. After the joint is finished, the ends of the pipe adjacent to the joint for a foot or two, on either side of the joint, or farther if the voltage drop is likely to be high, is painted over with a coat of pitch applied hot, and over this is wound a band of paper, cloth, or other fabric, which in turn is painted over with another coat of pitch, and so on until a layer of from 1 to 2 inches thick is obtained.

The expense of applying a coating of this character over a short length of pipe is small, and laboratory tests indicate that if carefully applied and made an inch or two in thickness it can be relied upon to remain effective for a number of years at least. That its life is limited, however, is indicated by the tests referred to in the

early part of this paper, which shows that moisture will slowly but surely penetrate the coating and when it finally reaches the surface of the pipe electrolysis begins and ultimately destroys the coating. The thicker the coating is made the longer time will be required for moisture to penetrate it and because of the higher resistance the slower will be the electrolytic action, even after the current path through the coating is established. Such a coating, if made an inch or more in thickness, would undoubtedly last in most cases as long as the pipe itself.

Another method of increasing the length of the leakage path around an insulating joint consists in surrounding the joint with a wooden trough several feet long and leaving a space of several inches on all sides of the pipe, this space being filled with pitch. This makes a very permanent insulating section and can be made as long as desired.

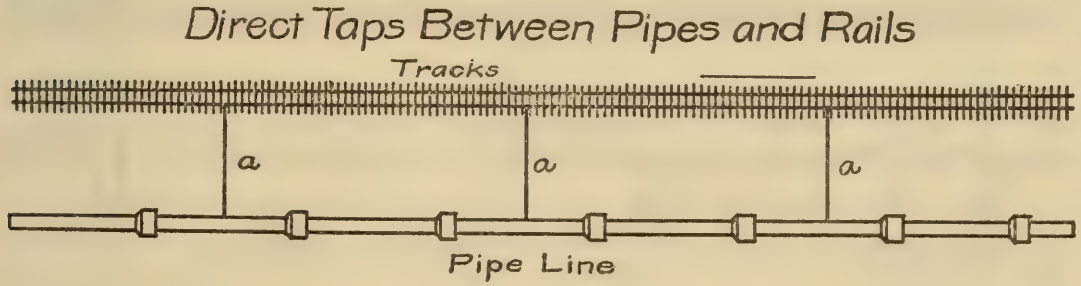


FIG. 23

9. PIPE DRAINAGE[5]

The system of electrolysis mitigation which has received wider application in this country than any other method is that which is best characterized as the pipe-drainage system. The essential features of this system consist in connecting conductors to the pipe system in the vicinity of the power stations or at other points where the pipes tend to become positive to the earth to take the current off through these conductors instead of permitting it to discharge directly into the earth.

(*a*) *Methods of Draining Pipes.*—Several forms of this system have been used. The simplest is that illustrated in Fig. 23. It consists simply in connecting short taps between pipe systems and railway track where the two run in close proximity to each

[5] This section revised March, 1918.

other and where the pipes are positive to the tracks. As a rule, the procedure in installing these taps has been to make a voltage survey throughout the affected district, and wherever the pipes are found to be strongly positive to the tracks a tie is put in connecting the pipes and tracks together, the intention being to install these ties at sufficiently frequent intervals to bring the pipe and track systems to practically the same potential throughout.

This system requires a minimum amount of copper but does not ordinarily permit of inspection, supervision, measurement, or control of current on the ties. It may be characterized as a blind system concerning which little is known after it is once installed. Unless very careful records are kept, it is practically

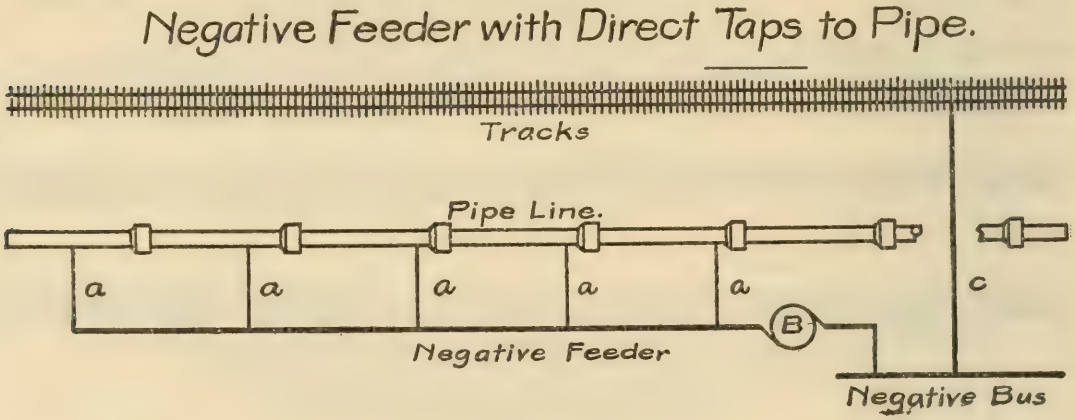


FIG. 24

impossible to locate all such ties if in after years it is desired to remove them for any cause.

Another difficulty with this system of multiple connections lies in the fact that the drop of potential on the pipes is always equal to the potential drop on the railway negative return between any points of connection to the track, and unless special precautions are taken to make the drop of potential in the railway tracks very low, this will necessarily lead to heavy current flow in the pipe, thus possibly giving rise to troubles as described below.

In order to overcome certain of the objections mentioned above, several modifications have been proposed, two of which are shown in Figs. 24 and 25. In both of these systems the primary object is to control and limit the drainage current. In

the first arrangement instead of tying the pipes directly to the tracks at frequent intervals a copper cable is run from the negative bus along the pipe line and tapped to it at frequent intervals by taps, *a*, *a*. This has the advantage over the system just described in that the pipe system is entirely independent of the tracks, so that the bad joints either in pipe or tracks between taps would in most cases be less serious.

The total current drawn from the pipes can be controlled by installation of the booster *B* in series with a negative feeder at the power house or, to some extent, by varying the resistance of the cable. Here, as in the preceding case, it is not practicable to control the distribution between the different sections of the pipe.

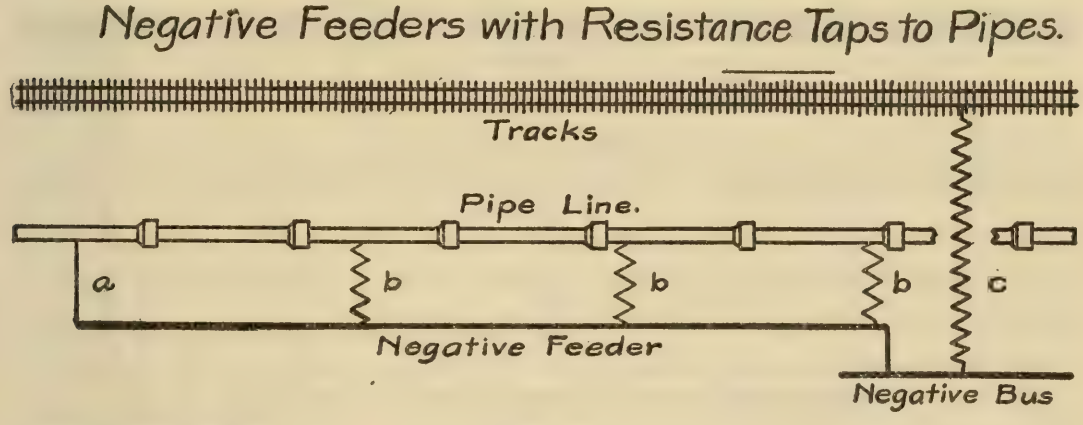


FIG. 25

The control of the total current by means of the booster will, however, be objectionable because of the complication and cost of the necessary booster equipment.

Another objection to this form of pipe drainage lies in the fact that the potential gradient on the pipe is the same as on the negative feeder, and because of this the current density in the copper cable will be very low unless the potential gradients along the pipe system is objectionably high. The result would be a very uneconomical use of copper, leading to high cost of installation in comparison with the benefits obtained.

In order to overcome certain of the objections mentioned above the modification shown in Fig. 25 might be used, although so far as we are aware, a system embodying these features has not heretofore been installed. In this case a cable is run along the pipe line as before, but instead of tying the cable directly to the pipe

line at frequent intervals, a direct connection to the pipe is made at the extreme end of the cable, *a*, and then at intermediate points *b*, *b*, connections are made between the cable and the pipe through suitably designed resistance taps.

It is possible by properly adjusting these resistances to secure a fairly equal distribution of current between the different taps regardless of the size of the feeder cable. In this way a better distribution of the current in the pipe system can be secured whereby a heavy current on the pipes at any point can be to a large extent avoided and at the same time the copper cable can be designed for maximum economy, and this greatly cheapens the installation. The method of pipe drainage most commonly em-

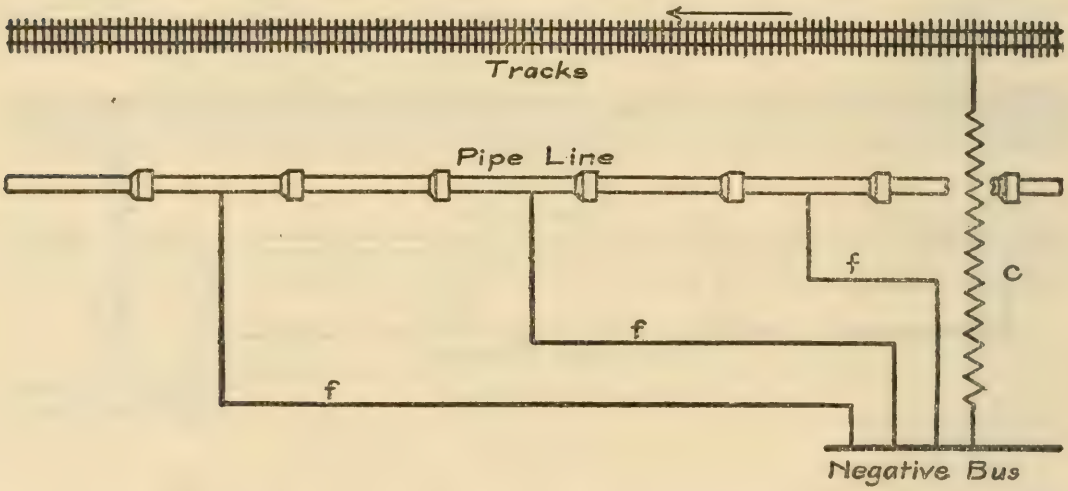


FIG. 26

ployed is that shown in Fig. 26. In this case the different feeders are designed to have practically the same resistance so that substantially the same current will flow in each one without any great difference of potential between the points at which they are connected to the tracks and, subject to this condition, the feeders are designed to give maximum copper economy. This, as a rule, involves a much greater drop on the feeders than is permissible along the tracks, and in order to prevent a large difference of potential between pipes and tracks near power house, and also to secure the necessary drop of potential to force the desired current over the drainage cables, a resistance tap *C* is installed the same as in Fig. 25. Where the resistance tap *C* is not employed, the drainage feeders should not be proportioned for equal resistance, but for approximately equal current flow.

(*b*) *Objections to Pipe Drainage.*—An objection which is inherent to pipe drainage is the fact that whichever form of it may be applied, it will necessarily increase to a greater or less extent the amount of current carried by the pipes.

Another objection is the possibility of damage at high-resistance joints. Lead-calked joints in cast-iron pipe lines sometimes develop comparatively high resistances, and if any considerable amount of current is flowing on the pipes, the drop on these high-resistance joints may become so great that the leakage current about the joint will be sufficient to cause rapid destruction of the pipe on the positive side of the joint. The term "high resistance," as here applied to pipe joints is used in a relative and not an absolute sense. A joint is said to have developed a high resistance when its resistance is considerably higher than the normal or average resistance of similar joints, although, as compared with cement joints, or specially prepared insulating joints, it may exhibit a very low resistance. Such joints may present considerable resistance to the flow of current on pipes and still transmit the current with very little destructive leakage, particularly in dry or otherwise high-resistance earth. The resistance of the leaded joints on any particular pipe line has, in general, been found to be uniformly low, although occasional joints of exceptionally high resistance are to be found in any piping system. A very different condition is established where an occasional cement or other type of high-resistance joint is inserted in a pipe line. If only a few such joints exist in a pipe line carrying a large current, they will have but little effect in limiting the current flow, and serious corrosion may, therefore, take place on the positive side of the joint.

Recent investigations of the Bureau in a number of cities, and inquiry and observations in connection with field surveys, have failed to bring to light, with few exceptions, any serious cases clearly attributable to joint electrolysis. In these investigations, tests for high-resistance joints were made over thousands of feet of pipe and those joints found to be of comparatively high resistance were uncovered and examined. A few joints were found which showed corrosion on the positive side, but in most cases not to such an extent as to shorten materially the life of the pipe. These investigations, taken by themselves, would tend to indicate that joint electrolysis is not so serious a matter as has been supposed.

It must be remembered, however, that the above evidence is of a negative character and can not be considered as conclsuive. The subject is still under investigation and will be taken up in subsequent reports.

Another objection to pipe drainage which must be reckoned with is the increased hazard from gas explosions, which exists whenever a gas pipe carrying an electric current is opened for repair or other reasons. To guard against this danger it is desirable to connect a copper wire or bond across the proposed break in any gas pipe to which drainage is applied. Failure to provide such a bond, or the accidental opening of the bond while the continuity of the pipe is interrupted, is liable to ignite escaping gas, with possible dangerous results to life and property.

One of the most serious objections to pipe drainage is to be found in the interchange of current between underground structures, resulting from unequal drainage. The drainage of one system of pipes will, of course, lower its potential with respect to neighboring metallic structures, thereby tending to injure the latter. This calls for drainage of the injured system which may, in turn, damage the first or other structures, and a competitive system of drainage is thereby established. This competitive condition might, to a large extent, be prevented by a system of unified drainage, whereby all underground structures in the community are drained as a unit and not independently by the several operating companies. Even if it were possible to employ such a system of drainage, it would be practically impossible to locate and eliminate all points of hazard. The danger of interchange of current between pipes and cable systems is not as great as between two different piping systems, such as water and gas, or two different water systems. The reason for this is to be found in the high resistance of the ducts which usually surround lead cables. Concrete, fiber, and vitrified clay ducts are of such high-resistance materials, and the cables make contact with them over such a limited area that the chance for leakage to or from a pipe outside of the conduit is considerably reduced, unless such ducts are filled with water. Under such conditions, or where in metal ducts, the drainage of lead cables beyond that necessary for protection is quite as objectionable

from the standpoint of the safety of adjoining metallic structures as the drainage of underground pipes.

A fundamental objection to pipe-drainage systems, however—and this applies to all methods applied only to the pipe systems—is the fact that they tend only to relieve the trouble rather than to remove the cause of it. In general, our study of the pipe-drainage method has convinced us that while it can under certain conditions be used to advantage as a *secondary* means of lessening the trouble, its installation in connection with most city networks as a *principal* means of electrolysis mitigation is an unwise procedure.

If the conditions are such that the potential gradients and overall drops on the track network can not, without too great expense, be reduced to sufficiently low values by some primary means of electrolysis mitigation, properly restricted pipe drainage may be used as a supplementary means of protection, in order to conduct the small remaining amount of stray current from the underground structures. This drainage should always be done under the supervision of a single authority or of a committee composed of representatives of the various utilities concerned, so as to eliminate as much as possible competitive drainage and to limit the amount of current drained from the different underground strucutres to a minimum consistent with their protection. We would point out, however, that there are special cases—such, for example, as that afforded by an interurban line paralleling water mains connected only to small networks—in which most of the objections mentioned above in connection with pipe drainage do not apply, and where neither insulated negative feeders nor the three-wire system would be feasible. In such cases pipe drainage may offer the best means of dealing with the problem.

10. SUMMARY OF DISCUSSION OF METHODS OF MITIGATION APPLICABLE TO PIPES

The discussion presented above relating to methods of mitigation applicable to pipe systems leads to the conclusion that of the various methods that have been tried none are suitable for general use as primary means of preventing electrolysis troubles. The methods of chemical protection, cement coatings, cathodic protection, and conducting coatings should be regarded as substan-

tially worthless in their present state of development. Surface insulation of pipes by means of paints or dips is not much more reliable, but insulation by putting the pipes in troughs or conduits filled with pitch may be used in special cases where the expense would be justified. The practice of placing all pipes as far as possible from railway tracks affords a certain measure of protection of which advantage should always be taken wherever practicable in laying new lines or relaying old ones, and the use of electric screens is often a valuable expedient in taking care of acute local cases of trouble in existing mains. These methods, with the exception of that relating to the proper location of pipes in new work, are suited only to special conditions, however, and are not usually to be considered as important factors in any general plan for electrolysis mitigation.

Pipe drainage is sometimes useful but should be used with proper restriction and with due precautions against setting up any dangerous condition either in the system drained or in neighboring systems. In general, in city networks where there are a number of independent underground systems to be protected, pipe drainage should be used as little as possible, the chief reliance being placed on mitigative measures applied to the railway negative return. The drainage of lead cable systems will, however, usually be desirable, but these should always be drained by means of suitable insulated-feeder systems so arranged as to drain the least practicable current from the cables in order that neighboring structures may not be subjected to unnecessary danger thereby. The most valuable mitigative measure that can be applied to pipe systems consists in the proper use of insulating joints, and the extensive use of such joints should be encouraged in new work and in making repairs. Precautions are necessary in their use, however, as set forth in the preceding discussion.

None of the methods of mitigation available for application to pipe systems are, except in special cases, to be recommended as principal means of mitigation, but rather as auxiliary or emergency measures, which may be used in connection with, and supplementary to, measures applied to the railway return systems for reducing stray currents to the lowest practicable minimum. Methods for accomplishing this end will be discussed in the next section.

IV. METHODS OF MITIGATION APPLICABLE TO RAILWAY NEGATIVE RETURN

None of the systems of electrolysis protection mentioned above have to do with the nature or condition of the street railway return circuits, and in the practical working out of such methods the railway return system is often ignored. The currents are permitted to flow away from the tracks without restriction, and the sole purpose of the methods outlined is either to prevent their entrance into the pipes or to provide means for their exit with as little injury to the pipes as possible. It would appear more logical to attack the problem by beginning at the source of the evil and prevent, to a large extent at least, the leakage of the currents from the railway return conductors into the earth. This is the more emphasized by the fact that in the past, where such mitigative measures have been applied to the pipes, the burden of providing the protection has usually fallen where it does not properly belong, viz, on the injured party and not on the party causing the injury. We shall now consider what measures may be applied by the street railway companies to their own properties with the view of removing, or at least greatly reducing, the cause of the trouble.

1. ALTERNATING-CURRENT SYSTEMS

The proposition to use alternating current for street-railway traction purposes need hardly be discussed here. If alternating current were used, the amount of electrolysis that would occur would in most cases be not more than 1 per cent of what it is with direct current. In the case of lead pipes the corrosion may be greater than this, but the experimental data available show that there is little likelihood of its exceeding this percentage under practical conditions.

The objections to the substitution of alternating current for direct current in the case of systems already installed in large cities are so obvious and so serious that the question needs no discussion, particularly since the problem of electrolysis protection can be taken care of by other means. In the case of suburban or interurban systems, on the other hand, where alternating current possesses certain advantages which for other reasons often justify its use, the fact that such a system will be comparatively free from electrolysis troubles is an additional argument in favor of its use.

This question of electrolysis, due to stray currents from interurban roads, is becoming increasingly important as pipe systems are installed or enlarged in small towns along the route, and particularly because of the steadily increasing number of pipe lines being installed throughout the country. In such cases the alternating-current system of traction may well be regarded as a satisfactory solution of the electrolysis problem, although at the present time the importance of this protection along interurban lines is not great enough to be by any means a deciding factor in the choice of systems.

2. DOUBLE-TROLLEY SYSTEMS

The double-trolley system of electric traction as at present used in Cincinnati, and the corresponding underground conduit systems as used in Washington and in parts of New York City, eliminate almost completely the danger of electrolysis, the small leakage which occurs being of no practical consequence. The chief objections to its use are the cost of installation and the increased operating difficulties which it involves. The cost of installation, which is very great, does not appear to be justified merely as a means of electrolysis protection, inasmuch as a very satisfactory degree of protection can be obtained by other and much more economical means.

3. USE OF NEGATIVE TROLLEY

Practically all street-railway systems in this country are operated with positive trolleys. Under such conditions the stray current is taken up by the pipes over a relatively large area and discharged within a comparatively small area, commonly called the positive area, near the power house. It is obvious, therefore, that the current density within this small positive area will be much greater on the average than in the much larger negative area. If the polarity of the trolley were reversed, the positive and negative areas would be interchanged without affecting to any considerable extent the intensity of the current at any point. We should then have a comparatively low average density of current discharge from the pipes throughout a much larger positive area. The total amount of corrosion would not be materially affected, but its dis-

tribution over the larger area would tend to reduce the intensity of damage at any particular point, so that the average life of the pipes would be increased and trouble would be much slower in developing.

Aside from the fact that in some cases the increased life of certain of the pipes might be such that they would endure until they would have to be removed anyway for reasons other than their failure, about all that can be said in favor of this proposal is that it postpones the time when serious trouble will develop. On the other hand, most engineers would prefer to have the trouble more localized, as it is under present conditions, where it can be more carefully watched and more effectively controlled. Furthermore, this reversal of trolley polarity will generally impose serious hardship on cable-owning companies which have already installed a drainage system for the protection of their cables. This method does not, therefore, appear to be worthy of serious consideration in the present instance.

4. PERIODIC REVERSAL OF TROLLEY POLARITY

Another proposal that has been advanced has for its object the attainment, as far as practicable, of the electrolytic conditions which prevail with alternating currents, without discarding the direct-current method of electric traction. If an alternating current flows from iron into soil, there is, during any half cycle in which the iron is positive, corrosion of the iron just as in the case of direct current, but during the succeeding half cycle the corroded iron is again plated out as metallic iron on the surface of the pipe. If the efficiency of both corrosion and deposition is 100 per cent, there will be no perceptible corrosion of the metal surface, and in the case of ordinary alternating currents this condition is very nearly realized in practice.

Experiments have shown that even with very low frequencies of reversals, such as once in 24 hours, a large measure of this effect persists, and the ultimate amount of corrosion is much less than would occur if the polarity is maintained always the same. It has therefore been proposed to reverse the polarity of the trolley at stated intervals, as, for example, once every 24 hours, as a means of reducing electrolysis troubles. If the reversals are made

with sufficient frequency to give effective protection, the method is open to the objection that it introduces a complication into operating conditions that does not appear to be justified by the benefits that would result, particularly where several substations are being operated in parallel. Where only a single substation is used, a reversal of polarity once in 24 hours would be entirely practicable and would undoubtedly be decidedly beneficial.

Extensive experiments at the Bureau of Standards show that with daily reversals of polarity the corrosion in the case of iron pipes at any particular point will be only about one-fourth as much as when the current flows continuously in the same direction. For lead pipes and cables the polarity would have to be reversed much more frequently in order to reduce the corrosion at any point to less than 50 per cent of that which would occur with unidirectional current.

5. REDUCING POTENTIAL DIFFERENCES IN THE UNINSULATED PORTION OF NEGATIVE RETURN

Turning now to a consideration of what may be accomplished in the way of providing an adequate return circuit for the railway currents we find a number of possibilities available. In considering these methods it is necessary to bear in mind that the fundamental condition to be realized in order to reduce the leakage of stray currents into the earth is *not the maintenance of the lowest possible resistance in the negative return but the minimum differences of potential between different parts of the grounded track network.*

The two conditions are not necessarily identical, depending as they do on the character of the negative return system used. The various possible methods of thus reducing track gradients to a satisfactory value all have for their primary object the taking of the current direct from the track through the agency of negative feeders, and they are therefore classed in one general group under the name of "track-drainage systems." These track-drainage systems present several separate practical embodiments, the chief of which are (*a*) the proper construction and maintenance of track to secure the full benefit of the conductivity of the rails, (*b*) grounding of tracks and negative bus, (*c*) the use of uninsulated negative

feeders in parallel with the rails, (*d*) the use of insulated negative feeders without boosters, (*e*) the use of insulated negative feeders with boosters, (*f*) the three-wire systems, and (*g*) the use of a proper number of substations so located as to take the current from the tracks so as to combine in greatest degree economy of distribution of power and reduction of leakage current from the rails. These different systems are discussed separately below.

6. CONSTRUCTION AND MAINTENANCE OF WAY

Proper maintenance of the track in order to secure high conductivity is everywhere recognized as a necessary condition in electric railway operation, but it does not always receive the attention that its importance justifies. In the matter of joints alone there is a very wide diversity of practice. In recent years, however, engineers have rapidly come to recognize the difficulty of maintaining a proper state of track conductivity by merely bridging the joints with short copper bonds. Such construction is still widely used, but it is finding much less favor than formerly, and in many systems, particularly where the traffic is heavy, these methods of shunting the joints are used, if at all, chiefly as secondary expedients. The tendency in such cases is to make the joint itself electrically continuous rather than to shunt around it, although both methods are not uncommonly combined.

The methods whereby more or less perfect continuity of the joints is obtained embrace the various types of welded joints such as electric welds, Thermit welds, etc., and those joints in which a second metal such as zinc and its alloys are employed to form the junction. Of these latter the well-known Nichol joint made by pouring molten zinc between the fishplates and the rail ends is one of the most effective, and has given very satisfactory service for a number of years. The zinc is poured in after the fishplates are bolted on and the expansion of the zinc which takes place on solidifying makes a firm and permanent contact between the fishplates and rail ends. Joints made either in this way or by any of the various welding processes have, as a rule, a lower resistance when new than an equal length of rail, and for the most part have given good satisfaction in service, although some trouble has been experienced, particularly in welded joints, due to parting of the

rails at the weld. Experience to date, however, indicates that these joints are very satisfactory in all cases where the tracks are laid in paved streets or otherwise suitably reinforced. As a precautionary measure, however, some engineers prefer to bond over all joints, also, and we understand that this is being largely done in St. Louis.

Cross bonding between the rails is also much resorted to as a means of maintaining track conductivity, and this is a very necessary precaution against the troubles arising from bad joints. If such cross bonds are properly installed and maintained at sufficiently frequent intervals, the deleterious effect of occasional bad joints is almost entirely eliminated. These cross bonds are usually placed at intervals of from 200 to 500 feet and these distances are sufficient if the cross bonds and rail joints are fairly well maintained.

All special work should be shunted by heavy cables capable of carrying all of the current passing over the tracks at that point. In many places this is the regular practice, but it is often neglected entirely or poorly maintained, and in some cases the drop across special work has given rise to very serious electrolysis. The remedy is so simple and effective that only carelessness can account for the existence of trouble of this nature.

The question of weight of rails is one that has not usually received the consideration which it deserves, particularly in the case of the T rails. At the present price of girder rails there is very little difference between the cost of rail and copper of the same conductivity. The conductivity of steel rails varies considerably, but on the average it will be about one-tenth to one-twelfth that of commercial copper. Hence, at the former figure with copper at 17 cents per pound and rails at $39 per ton the cost of a given conductance will be about 10 per cent greater if obtained by using copper cables in parallel with the rails than if it is obtained by the use of heavier rails. In the case of T rails costing $28 per ton the cost of a given conductance in steel rails will be about two-thirds that for copper. This is on the assumption that the extra labor cost of laying the heavier rails will about equal the cost of laying the copper cables. As to whether or not this is true will depend largely on local conditions, so that the above figures are only approximate.

An important factor which should be considered here, however, is the reduction in track and rolling stock maintenance charges that accompany the use of heavier rails. This is often sufficient to justify the extra expense of the heavier rails quite apart from any consideration of their higher conductance, and largely for this reason there has been a general tendency in recent years to use heavier rails. When we consider this fact in connection with the increased conductance of such rails there would appear to be good reason for using somewhat heavier rails than traffic conditions would usually call for in those regions near the power houses where it is important to secure higher conductance than would be afforded by the usual weight of rails.

The rail weights used in most large cities range for the most part between 80 and 120 pounds, so that we may consider that the approximate average weight is but little more than 100 pounds per yard. A double track of these rails having good joints has a conductance equivalent to about 4.5 million circular mils of copper. Standard rails are now rolled and in practical use weighing 137 to 139 pounds per yard and would have a conductance of about six and one-quarter million circular mils, or an increase over that of the average rails equivalent to about one and three-quarter million circular mils. It would therefore appear to be worth while in some cases, when tracks are being relaid near the power stations, to consider seriously the advisability of using much heavier rails than are usually adopted, the combined effect of improved track conditions and increased conductance being sufficient to justify the additional expense.

A properly constructed and drained roadbed is also a very effective aid in reducing the leakage of stray currents from the rails. The amount that can be accomplished in this way will, of course, vary greatly with varying conditions so that no specific recommendations can be made here, other than to point out that since the conductance of the leakage path is mainly dependent on the amount of moisture which is contained in the material forming the roadbed and the earth beneath, any construction which tends to reduce the average moisture content therein will reduce in corresponding degree the magnitude of the leakage currents. Indeed, we have made tests on long lines of track without inter-

sections to cause complications, in which it was found that leakage from the rails had been almost entirely eliminated, the reason being that the road was so constructed that the leakage path from rails to earth was on the whole comparatively dry. We believe that much more could be accomplished by this means than is commonly supposed without materially increasing the cost of construction, although it must not be regarded as a satisfactory primary means of electrolysis mitigation.

7. GROUNDING OF TRACKS AND NEGATIVE BUS

The grounding of the negative bus or the tracks near the power house was one of the earliest expedients resorted to for the purpose of reducing the resistance of the negative return. Because of the decided tendency for such grounds to increase the flow of leakage current from the tracks it was early recognized that they might tend to increase electrolysis troubles, and in the majority of cases these ground plates have been abandoned. There are, however, a good many cases where such grounds still exist, so that their bearing on the electrolysis situation is an important matter. During the last few years, also, it has been seriously recommended by certain well-known engineers that this expedient of grounding tracks be carried much further, and, in fact, used as a means of eliminating electrolysis.

The method of procedure proposed by the advocates of this system is to lay ground plates several feet below the track and at frequent intervals throughout the stystem so as to secure as nearly as possible the perfect grounding of the tracks at all points. This proposal has been based chiefly on experiments which have been performed with small electrodes buried in the earth which showed that most of the resistance between such electrodes and the earth was found to be in the region very near to the electrode, owing to the small cross section of the current path at such points. From these experiments the conclusion was drawn that at a distance of 3 or 4 feet from such an electrode the cross section became so great that the resistance practically disappeared. It was therefore thought that if frequent ground plates were laid 3 or 4 feet below the track and connected thereto, the large cross section of the path offered for the discharge of current into the earth would

cause the resistance of the negative return practically to disappear, and consequently the drop of potential in the earth would be so small that no appreciable current would be picked up by the pipes.

Our own investigations on this subject, which have comprised experiments with electrodes both of the size used in the investigation above referred to, and also with much larger ones, which are more comparable with conditions which actually exist in railway systems, and also the results of voltage surveys made remote from electrodes that might serve as sources of stray currents, have convinced us that the theory on which this method of protection is based is erroneous, and that the stray currents that would be introduced into the earth by the proposed ground plates along the track would greatly aggravate the trouble from electrolysis. We would strongly urge, therefore, that grounds of all kind, whether along the track or the negative bus, be altogether eliminated in every case.

8. UNINSULATED NEGATIVE FEEDERS

A typical form of uninsulated negative feeder system is shown in Fig. 27. It will be seen that this consists essentially in running

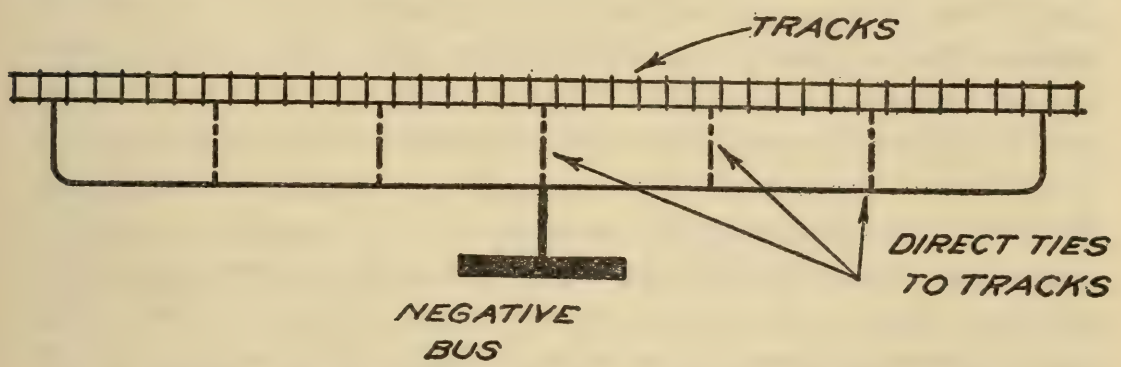


FIG. 27.—*Diagrammatic representation of uninsulated negative feeders*

feeders out from the negative bus to various points of the track. Each feeder may be connected to the tracks at a number of points, and the tracks nearest the power house are connected directly to the negative bus through low-resistance cables. The return cables are therefore directly in parallel with the rails, and the current divides between the rails and the feeders inversely as the resist-

ance of the various paths. In so far as the principle of operation is concerned it will be evident that it is of secondary importance whether the feeders are actually provided with insulation or not. The fact that they are connected directly to the tracks at both ends, and in some cases at intermediate points, also makes them essentially the same in principle as uninsulated feeders, and they are here so classed whether they are actually laid in the ground bare, provided with insulation, or run on poles overhead. The only effect of insulation on the underground feeders connected in parallel with the tracks would be to reduce slightly the leakage resistance between tracks and ground.

It is obvious that when copper cables are connected in this way potential gradients on the cables will always be the same as that on the rails in the section in parallel therewith. It is shown in another part of this paper that under average conditions in this country good electrolysis conditions require that the all-day average potential gradient in the tracks should in general not exceed 0.3 to 0.5 volt per thousand feet with correspondingly higher values for peak-load periods. These gradients on copper cables would correspond to from 27 to 45 amperes per million circular mils. It is well recognized, however, that the most economical all-day average current density for railway feeders lies between 200 and 300 amperes per million circular mils. The most economical current density would therefore usually be found to be seven or eight times the maximum value required for good electrolysis conditions. It is evident, therefore, that to secure sufficiently low gradients by reinforcing the conductivity of the rails by simply putting cables in parallel with them would be extremely wasteful and not worthy of serious consideration. Hence, some other method must be used if a reasonable degree of economy is to be attained. Such economy is afforded in a large degree by the insulated negative feeder system described below.

9. INSULATED NEGATIVE FEEDERS WITHOUT BOOSTERS

(*a*) *Development of the Insulated Negative Feeder System.*—The use of insulated negative feeders for the purpose of securing low potential drops in the negative return independently of the drop in the feeders themselves has until recently received but little

attention in this country, although the principle of their operation and their advantages were pointed out many years ago. The first to suggest the use of insulated feeders instead of uninsulated feeders for electrolysis mitigation was Isaiah H. Farnham, who published an article in Cassier's Magazine in August, 1895. In this paper the fundamental principles of the insulated return feeder system without boosters were clearly set forth, and in view of the more recent developments in this direction it seems remarkable that Farnham's paper did not attract more attention at the time of its publication. This paper is of such fundamental character and reveals such a clear understanding on the part of the author of the principles of the insulated feeder system that we reproduce a large portion of it in the appendix of this paper.

Some years after the appearance of the paper above referred to, a paper was presented before the Institution of Electrical Engineers in Great Britain by A. P. Trotter, in which the principles of the insulated feeder system were set forth in a very able manner, and soon thereafter insulated feeders became widely used in various cities in Great Britain, and at a later date on the Continent, although for the most part they were used in connection with negative boosters.

In this country practically no progress was made for a good many years toward the utilization of the advantages of insulated negative feeders, attention having been almost entirely directed to the application of other methods of mitigation, chiefly those applicable to underground pipe and cable systems.

About 10 years ago a system embodying in some degree the principles of the insulated feeder system was installed in Richmond, Va., and is still in successful operation. In 1907 a paper by George I. Rhodes before the American Institute of Electrical Engineers called attention again to the advantages of insulated feeders for reducing potential gradients in the railway negative return. However, with the exception of the system above mentioned, installed in Richmond, and a similar system installed on portions of the Interborough Rapid Transit Co.'s lines in New York City, practically no progress was made in the direction of the practical application of this system until within the last two or three years. About two years ago the American Railways Co., of Philadelphia,

installed a system of this kind on its Springfield (Ohio) property, and has since installed similar systems on a number of their other properties.

A short time afterwards a similar system was installed by the United Railways Co. of St. Louis at its Ann Avenue substation. These two systems in Springfield, Ohio, and St. Louis, Mo., have been given wide publicity, and during the last two or three years many systems of a similar character have been installed in various cities throughout the country. The progressive attitude adopted by the American Railways Co. has done much to call attention to the advantages of the insulated feeder system and to popularize its use, and it is due largely to the important work of this company that the advantages of the insulated negative feeder

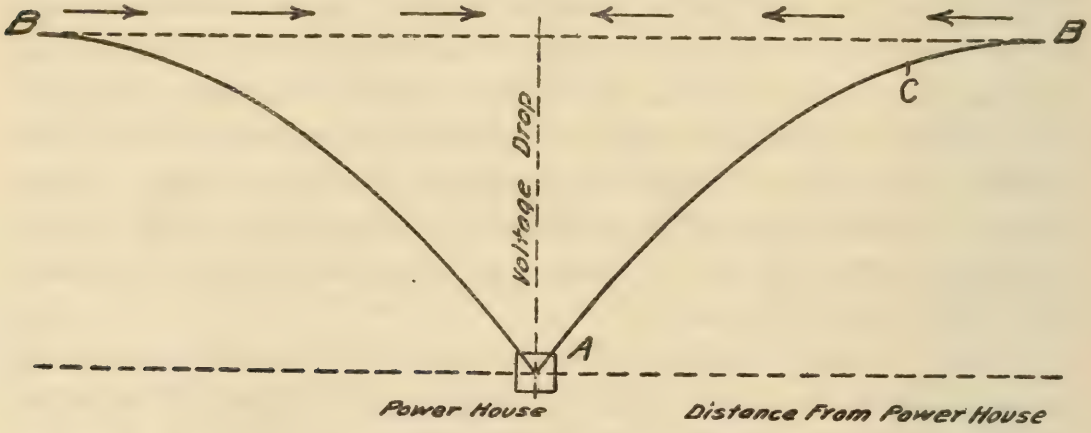


FIG. 28

system are rapidly becoming appreciated by railway companies throughout the country.

(*b*) *Types of Insulated Negative Feeders.*—In the insulated negative feeder system, instead of tying the tracks directly to the negative bus and depending on the tracks and such copper as may be in parallel therewith to return the current to the power house, the connection at the power house is either removed or given a suitable resistance, and insulated feeders are run from the negative bus to various points on the tracks, as shown diagramatically in Fig. 31. By this means several important results may be achieved. In the first place, the current being taken off the rails at numerous points, high current densities, and consequently high potential gradients in the rails, can be avoided to any desired degree. In the second place, by so designing the system that the drop of

potential on all of the feeders is the same, the current flow in the tracks can be so subdivided that the direction of the flow will be reversed, thus preventing the accumulation of large potential differences between points on the tracks which are some distance apart.

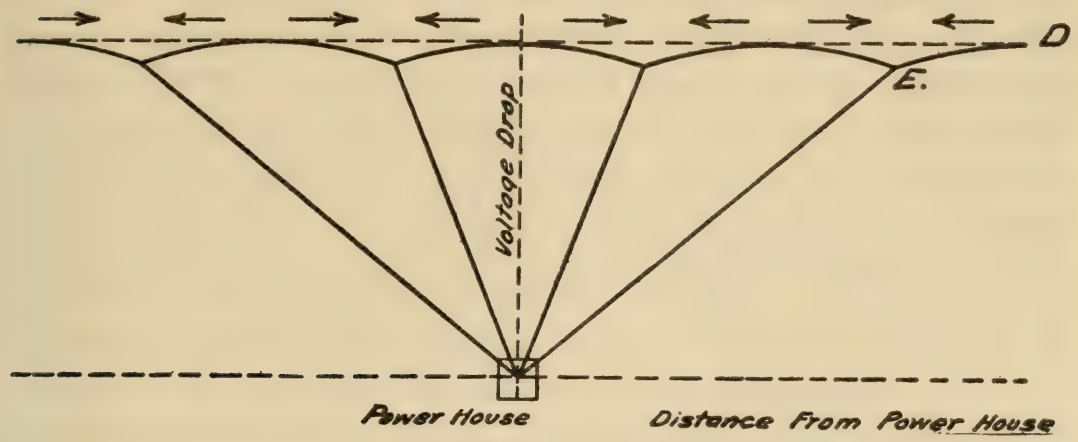


FIG. 29

Further, it will be evident that in this case the actual drop of potential in the different feeders is of little importance so far as electrolysis protection is concerned, so long as it is nearly the same in all. We can thus impose any desired potential restriction on

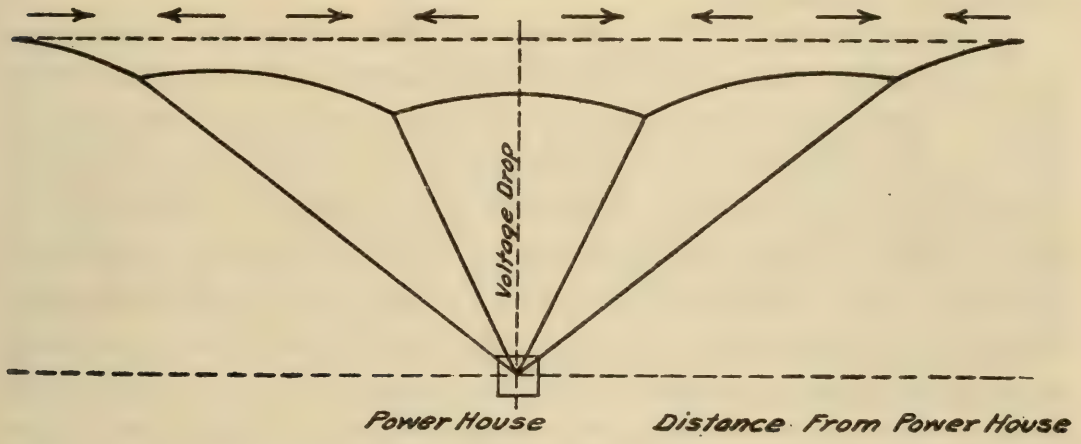


FIG. 30.—*Effect of insulated feeders in reducing rail gradients*

the track and still be free to design the feeders to give maximum economy, which we can not do when the feeders are connected in parallel with the tracks, as has been the common practice in the past in practically every American city. A graphic representation of what can be accomplished by using a system of insulated feeders of this sort is shown in Figs. 28, 29, and 30.

Fig. 28 shows the arrangement of the negative return in which any feeders that are used are connected directly in parallel with the track throughout, and a uniform distribution of the load on the line is assumed. The arrows show the direction of the current flow, and the curved line *AB* shows how the potentials of the rails vary from point to point, the potential curve becoming steeper and steeper as the power house is approached. With uniform distribution of the load, as here assumed, and uniform track conductivity it can be readily shown that this potential curve is the segment of a parabola. Fig. 29 shows the same system with insulated negative feeders run from the negative bus to four points on the track, two in either direction, and so designed that the drop of potential is the same on all during average load conditions. Here also the curved lines represent the potentials of the tracks from point to point, and, as in Fig. 28, the curves are segments of parabolas. The portion *DE* of Fig. 29 corresponds exactly to the portion *BC* of Fig. 28. It is seen that the current flow in the tracks is here so subdivided that the total over-all potentials become very small, and consequently the tendency to set up large differences of potential between the rails and surrounding structures is practically eliminated.

An examination of Figs. 28 and 29 shows that the maximum potential difference in the rails is reduced to one-sixteenth of its former value by the installation of only two negative feeders on each side of the station. It is evident, of course, that this great reduction in the potential difference in the tracks is obtained at the sacrifice of track conductance, of which little use is made in the latter case. Between these two extremes any desired compromise can be obtained; that is to say, instead of making the drop on all of the feeders the same, we may make the drop on the feeders lower as we approach the power house, thus making a continuous gradient equal to the maximum allowable gradient all the way to the station. We can thus utilize the conductance of the tracks to the limiting extent consistent with satisfactory electrolysis conditions. This will result in a more economical installation, but at the expense of greater over-all potential differences in the track return system, even though the limiting potential gradients in

the track may be the same. This type of feeder system is shown diagrammatically in Fig. 30.

This latter plan is often more economical than the plan shown in Fig. 29, and it is sometimes to be recommended where conditions are such that there is a large track conductance to be availed of. Wherever the track conductance is small, however, so that most of the current will have to be returned by the feeders anyway, the equal-drop system is to be preferred, since electrolysis conditions will be better and the difference in cost not very great. A still further modification of the insulated feeder system will generally be found to be desirable. In this modification, instead of running several independent feeders in one direction from the power house, a single large feeder is run along the line and connected to

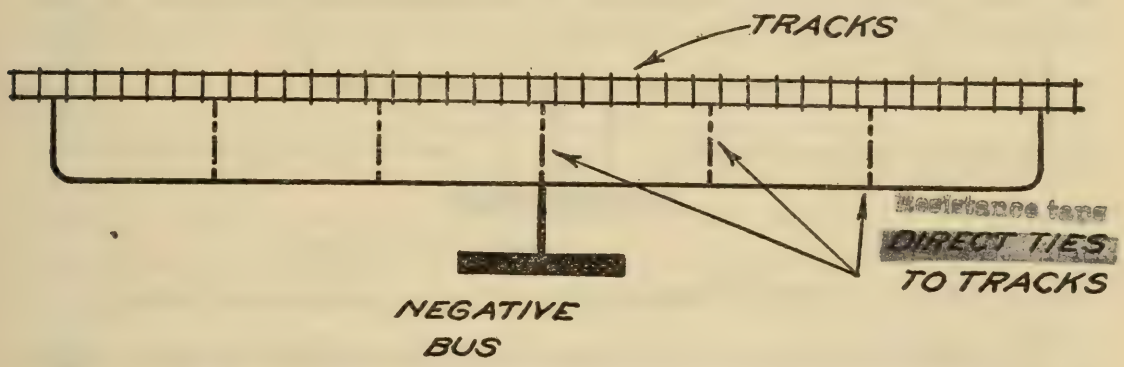


FIG. 31.—*Diagrammatic representation of insulated negative feeders*

the tracks at suitable points by means of resistance taps. This system is shown diagrammatically in Fig. 31. It has the advantage of simplicity of line construction, cheaper first cost and maintenance, due to running one large feeder instead of several small ones (where the total feeder area is not great), and it also has the advantage of bringing back a much larger load on the single feeder, which results in a less variable current, and this makes possible a more economical use of the negative copper.

From the foregoing it will be apparent that the economy of using insulated negative feeders as compared wuth uninsulated feeders in parallel with the tracks is so great, particularly when it is necessary to maintain the voltage drops in the track at very low figures, such as is usually necessary for electrolysis protection, that only insulated negative feeders can be considered seriously,

and they should always be installed in lieu of uninsulated feeders when the conductance of the tracks is not in itself sufficient to carry the current without excessive voltage drop.

(*c*) *Calculation of Insulated Negative Feeder System.*—It is desirable to state briefly here the methods of procedure in laying out the design of insulated negative feeder systems. A careful study is first made of the load distribution over the entire territory supplied by the station under consideration, and from this study the most natural points for taking off the current are selected and the number of amperes that must be taken off at each point in order that the current in the rails shall not exceed a predetermined value is determined.

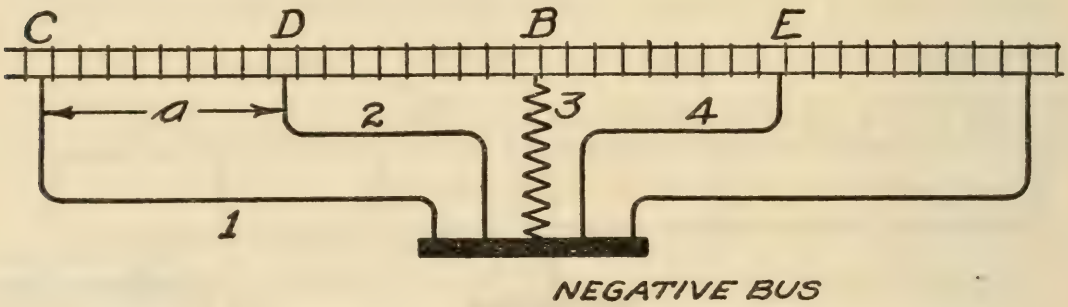


FIG. 32.—*Diagram illustrating calculations of insulated negative feeders*

A preliminary value of potential drop in the first feeder, which is usually one of the largest and most important ones, is then assumed, and from this drop and the current to be carried by the feeder, together with its length, the cross section of the feeder is calculated. When this is done, all of the other feeders must be designed consistently with this so as to avoid potential gradients in the tracks greater than the value determined upon as the limiting allowable average gradient.

Beginning thus with feeder No. 1, Fig. 32, we find that the voltage drop to be allowed on feeder No. 2 is the drop on No. 1 less the allowable drop on the tracks over the distance (*a*) between the points at which the two feeders connect to the rails. For instance, if the assumed drop on feeder No. 1 is 15 volts and the distance between the two taps is, say, 1200 feet and we are permitting a maximum drop of one-half volt per 1000 feet in the tracks, the average gradient between *C* and *D* will in general be less than this figure, depending upon the amount of load origi-

nating between these points. The average value of this can be determined from the car schedule. Assuming it to be 0.4 volt per 1000 feet, for example, the total average drop between *C* and *D* will be 0.48 volt. The total drop on feeder No. 2 will therefore be $15-0.48=14.52$ volts. From this value and the current assigned to feeder No. 2 its cross section can be calculated, the length, of course, being already fixed.

We proceed in a precisely similar manner to calculate any other feeders on this same line between feeder No. 2 and the power house, including the resistance tap *B* at the power house. It is then necessary to work outward from the power house in calculating the remaining feeders. For example, if the voltage drop on the power house tap has been found by the above-described procedure to be 12 volts, the drop on feeder No. 4 will be 12 volts plus the allowable drop on the tracks between the power house tap and the point *E* at which the feeder is connected to the tracks, and so on for other feeders more remote from the power house.

Sometimes the cross section of the feeders as thus calculated will be too small to carry the required current without overheating, and when this is the case the feeder must be made sufficiently large to carry the current and an additional resistance inserted preferably at or near the power house in order to give the necessary voltage drop. When this calculation is complete for all the feeders we are ready to determine whether the original assumption made in regard to the voltage drop on the first feeder was the one that would give approximately the most economical installation over the entire system. To determine this we sum up the total cost of the feeders installed and determine the proper annual charge, including interest, taxes, and depreciation, and also calculate the total annual value of the energy lost in the feeders and resistance taps. If these are approximately equal, the voltage drop assumed was the proper one. If, however, the annual charge on the feeder system is less than the cost of lost energy, the voltage assumed is too high (and vice versa) and a correction must be made.

This correction may be very easily and simply supplied without recalculating the feeder system as in the first instance. For ex-

ample, if the annual cost of the feeders is found to exceed that of the energy lost by 20 per cent, we must increase the voltage drop by approximately 10 per cent, and reduce the area of the feeders by about 10 per cent, which change will bring the cost to approximate equality, a condition for the most economical installation. If E_1 is the original voltage drop calculated for any given feeder and E_2 is the weighted mean voltage drop for all feeders, then the increase of voltage on any feeder being $\frac{E_2}{10}$ we must reduce the cross section of the feeder by the factor $\frac{E_1}{E_1 + \frac{E_2}{10}}$. The value of E^1 in each case is the initial voltage drop calculated for that particular feeder, so that each feeder is corrected by a different factor. When the correction is made in this way there is no change in the potential gradients and current distribution assumed for the rails.

(*d*) *Effect of Concentrated Loads on Effectiveness of Insulated Feeders.*—The view has been taken by some engineers that while the insulated negative feeder system works out very well when applied to a fairly well distributed load it fails to show any appreciable advantage when applied to conditions where the load is concentrated at a few points, such as is usually the case on an infrequent schedule. While this is true when we consider the maximum values of potential drop between different points of the negative return, it is not true if we are considering the effectiveness of the electrolysis protection afforded.

Under the extreme condition of a concentrated load moving back and forth along a track provided with insulated negative feeders, the direction of the leakage currents will be periodically reversed. Experiments have shown, however, that if the period of the cycle is not more than 10 to 15 minutes, or even longer, the actual amount of corrosion that occurs is only a very small fraction of that which would take place if voltages of the same magnitude existed in the negative return and always in the same general direction. For this reason this negative feeder system, when used in connection with a concentrated load, will always give much greater reduction in the actual amount of the electroly-

sis damage than it does in the actual voltages which exist from time to time between different points in the negative return. In consequence of this fact, it may be stated that so long as improvement in electrolysis conditions is the object sought, the insulated negative feeder system may be regarded as being quite as applicable to a system having concentrated loads moving back and forth along the line at frequent intervals as to a system in which the loads are more or less uniformly distributed along the line.

10. INSULATED NEGATIVE FEEDERS WITH BOOSTERS

(*a*) *Direct Boosters.*—The insulated negative feeder system described above, because of its symplicity and economy will be found most suitable for practically all cases where the feeding distances are not too great. Cases are frequently encountered, however, in which one or more of the lines are supplied over such a great distance that serious difficulties are encountered. For instance, if the power house is supplying a network of lines near the station, insulated feeders may be made to take care of this area without requiring a voltage drop on the feeders or the power-house tap of more than perhaps 10 to 20 volts. At the same time one or more very long and perhaps heavily loaded lines may extend from the network, and if an insulated feeder, as above described, is to be used to take care of this line also, it would be necessary to use a very heavy feeder in order to keep the voltage drop comparable with that on the feeders running to the local network, or else a high resistance would have to be inserted in series with the latter.

The former alternative would involve a prohibitive charge for copper, while the latter, by making all of the current from the network return over a relatively large voltage drop in the power-house tap, would give rise to large power losses. These difficulties can be avoided by designing both the local feeder system and the long line on the basis of the most economical size of cables and connecting in series with the long line a booster designed to supply the voltage necessary to force the required currents over the long feeder. This booster will consist of a direct-current generator of suitable voltage to take care of the peak-load drop of the feeder,

coupled to either a 600-volt D. C. motor or an induction motor, according to circumstances. By the use of such a booster it will sometimes be possible to save enough in copper investment or power losses to more than compensate for the losses in the booster and the installation cost and complication which attend its use.

(*b*) *Inverted Boosters.*—Instead of connecting a direct booster in series with the long feeder, as above described, a similar result can be accomplished by insertion in series with the shorter feeders supplying the local network an "inverted" booster. This would consist of a series-wound motor connected in series with the local feeder system, this motor being used to drive a constant-speed generator connected to either the D. C. or A. C. bus bars. If the latter, an induction generator would be preferred. With this arrangement the speed would be held substantially constant, and hence the counter emf of the series motor would be proportional to the current, which condition would be necessary for maintaining the proper balance between the two feeder systems. A little consideration will show that when such an inverted booster is used in lieu of a resistance tap, instead of the energy being dissipated in the resistance tap, the excess energy over that required to supply the booster losses is delivered back to the D. C. or A. C. bus bars through the generator driven by the series motor.

It is evident that the operating characteristics obtained from these two booster systems will in general be substantially the same. The choice between them will therefore depend mainly on the relative load in the two parts of the system. It is evident that if the greater part of the load is on the long feeder, the use of a direct booster in this feeder would require a larger and more expensive machine as well as greater power losses in the machine itself than if the inverted booster were used in series with the relatively small load in the local network. Hence, if the load in the local network is the smaller, an inverted booster would be cheaper, while if the greater part of the load originates in the local system a direct booster in the long feeder would be indicated. In the majority of cases, however, the insulated feeder system without boosters as described in the preceding section is found to be as cheap or cheaper than either of the booster systems, and is generally to be preferred because of its greater simplicity.

11. THREE-WIRE SYSTEMS [6]

(*a*) *Extent of Adoption.*—This method of power transmission is that commonly used for city light and power and known as the Edison three-wire system. Until recently it has not been employed for street railway work in this country, although it has been in use in Nuremberg, Germany, for a number of years. In the last few years it has received some attention in America, and is now in operation in some portions of Los Angeles, Omaha, Wilmington (Del.), and Milwaukee. Springfield (Mass.), Seattle, and other cities are also preparing to adopt it.[7]

The Los Angeles installation has been in operation for nearly three years and plans are now under way to extend the system to include several additional station districts. In Omaha a trial installation in one station district was made early in 1917. After several months' trial with the experimental installation, the main station district was converted for three-wire operation and has since been so operated. A trial installation was made in Springfield, Mass., in 1916, the results of which were sufficiently encouraging to justify the permanent installation which is now being made.

The cause for the prominence which this system of electrolysis mitigation has so recently attained is to be found largely in the high price of copper and other materials and the difficulty of financing new work. These factors have made so difficult the employment of extensive insulated negative feeder systems, that railway companies confronted with the problem of electrolysis mitigation have been forced to adopt other measures requiring a smaller initial expenditure of capital.

(*b*) *Parallel Three-Wire System.*—The three-wire system may take two different forms the same in principle but differing radically as to the arrangement of the feeder system. One of these is directly analogous to the ordinary three-wire system of lighting and is called the parallel three-wire system. The typical arrangement for the case of a double-track line using this system is shown in Fig. 33. Here one trolley is negative and the other positive,

[6] This section revised March, 1918.

[7] Articles descriptive of the three-wire system are to be found in the Electric Railway Journal as follows: "Three-wire operation in Los Angeles," Feb. 26, 1916; "Three-wire operation in Omaha," Nov. 10, 1917; and "Sectionalization of overhead for three-wire operation," Dec. 8, 1917.

the tracks being neutral. It is evident that only the difference in the load on the two sides of the line returns to the power house on the track, although there may at times be heavy circulating currents flowing between cars in short sections of track. If the cars run at frequent intervals, however, such circulating currents will not have to flow over sufficiently great distances in the tracks to set up nearly as large potential differences therein as would exist with the same loads under the ordinary track-return system. The result would be that where load conditions are reasonably favorable for the work of the three-wire system, large reductions in potential drops in the negative return could be secured.

A single-track line with two overhead trolleys, one positive and one negative, can also be used, or the two tracks may be on differ-

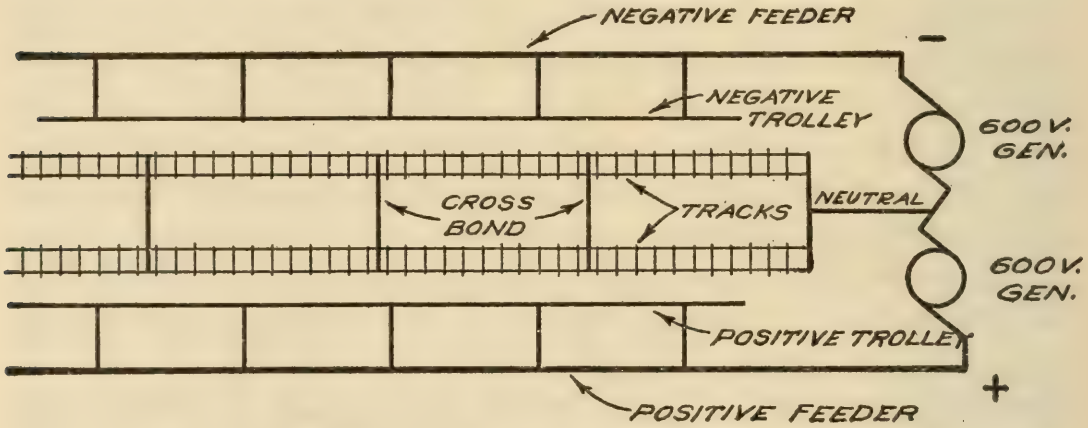


FIG. 33.—*Parallel three-wire system*

ent streets, the trolley on one street being positive and that on the other negative. The latter, however, is open to the objection that since the current would generally tend to flow in one direction in the tracks on one street and in the opposite direction on the other, frequent cross-bonding becomes very important, and unless the two lines are close together this would become quite expensive.

Where a number of tracks on parallel streets are intercepted by frequent cross-town lines, alternate tracks can be arranged for opposite polarity and the cross-town tracks made to act as equalizing busses. This arrangement would offer an approach, on a large scale, to the conditions just described for parallel three-wire operation. Good bonding of the cross-town lines would be a

necessity, however, in order to permit of free interchange of current between the several parallel tracks. Such a condition was found in New Orleans, where the Bureau, after supervising an electrolysis survey in January, 1918, recommended the adoption of a three-wire system in which the trolleys on a number of parallel streets were to be alternately positive and negative. Several cross-town tracks at intervals of from 3000 to 4000 feet exist, which should provide ample capacity for interchange of current between the positive and negative cars.

(*c*) *Sectionalized Three-Wire System.*—While almost perfect electrolysis conditions could be obtained with the parallel three-wire system, the difficulty of thoroughly insulating the two trolleys from each other is so great that the sectionalized three-wire sys-

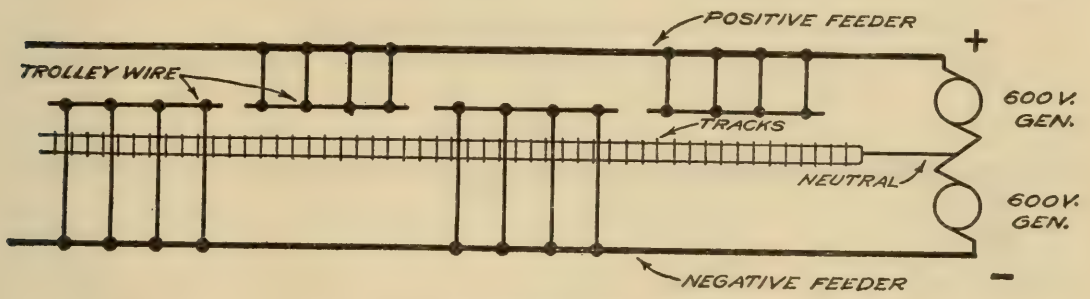


FIG. 34.—*Sectionalized three-wire system*

tem, now to be described, is considered the more practicable and has therefore been employed in all installations which have come to our attention. It is shown diagrammatically in Figs. 34 and 35.

In this form the feeding district is divided into sections, and alternate sections are supplied by feeders running from the positive bus, while the remaining sections are supplied by feeders from the negative bus, the difference of potential between the two busses being 1200 volts. In this way the existence on the same portion of the street of two trolleys having a high difference of potential between them is avoided. The tracks as before serve as the neutral and convey the current from the cars in one section to those in the adjoining section and return the unbalanced current to the power house. In Fig. 35 nine cars are shown, six of which are supplied from a positive and three from a negative generator. It is seen that current enters the three negative cars from the rails instead of from the trolley. The current returning to the station

is that from only three cars instead of from nine, as would be the case under ordinary or two-wire operation. The load can, of course, be divided in any desired proportion between the positive and negative generators.

The advantages of this form of three-wire system are (1) that it separates the positive and negative trolley sections, keeping them on different portions of the line, and (2) any system in which the substations have two positive busses and two or more generators can quickly and cheaply change to this system, the only requirement being to sectionalize the feeding and trolley system in such a way as to properly balance the load.

Both of these three-wire systems require for satisfactory operation a fairly well-balanced load, and hence they will operate more

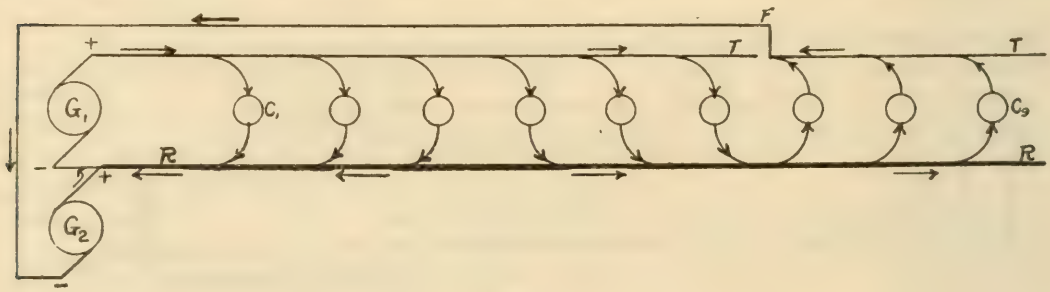
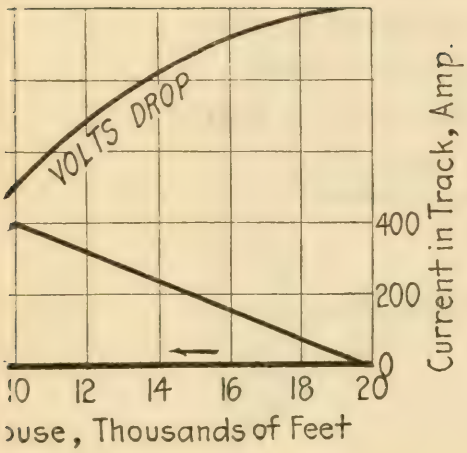


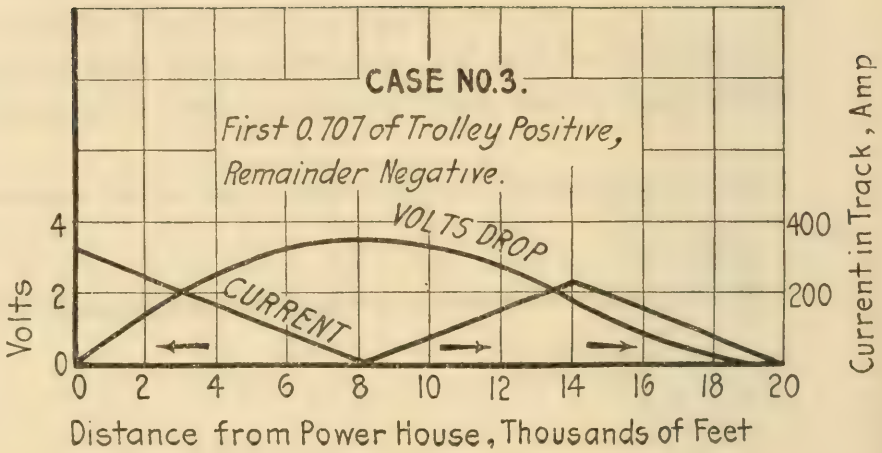
FIG. 35

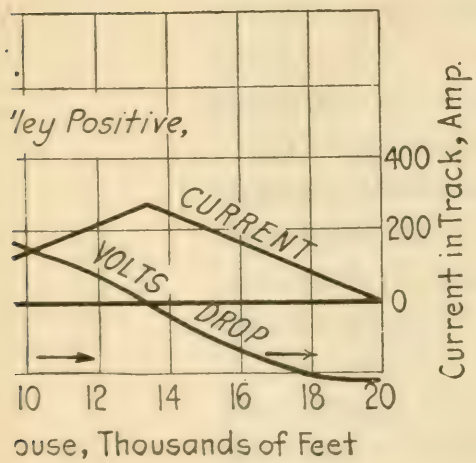
satisfactorily in sections where the schedule is frequent. For infrequent suburban or interurban service, voltage fluctuations at the cars would be serious, giving rise to unsatisfactory car service and car lighting and undoubtedly increasing the maintenance cost of the car equipment.

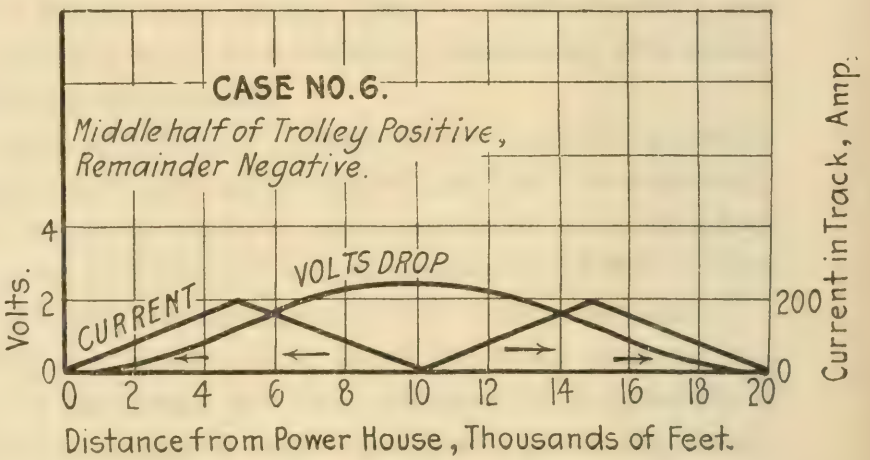
(*d*) *Sectionalization of Trolley.*—Electrolysis conditions are so strongly affected by the trolley sectionalization that it is extremely important for the engineer wishing to experiment with or adopt this method of power distribution fully to understand the several effects produced by each arrangement of the trolley sections.

The curves in Fig. 36, cases 1 to 6, show the track current and the voltage drop in the track for five different arrangements of the trolley sections as compared with conditions prevailing under normal or two-wire operation. The curves are based on the following assumptions: Twenty thousand feet of double track, the resistance of which is taken as 0.0025 ohm per 1000 feet (100-pound rails, well bonded); a load of 40 amperes per 1000 feet of

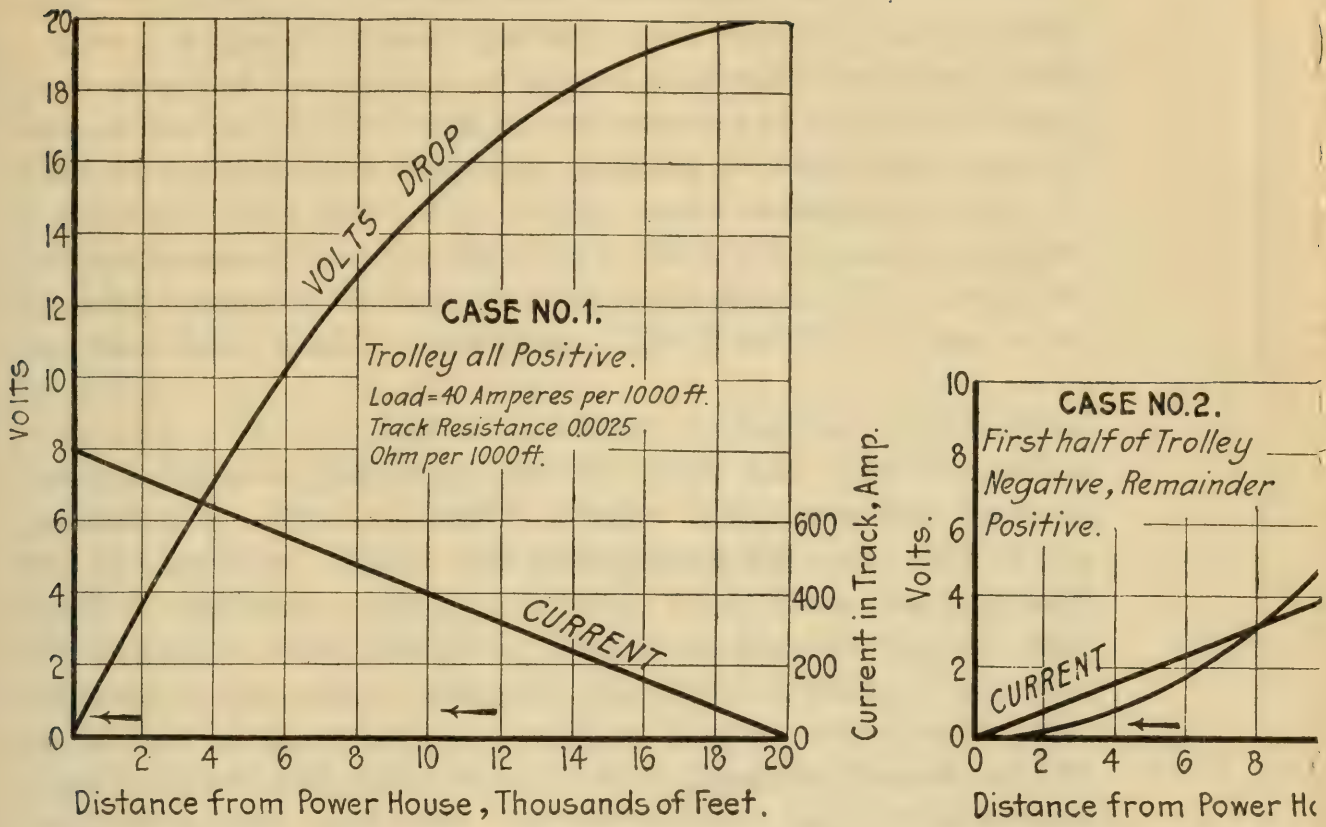

VOLTS DROP
400
200
0
Current in Track, Amp.
10 12 14 16 18 20
ouse, Thousands of Feet

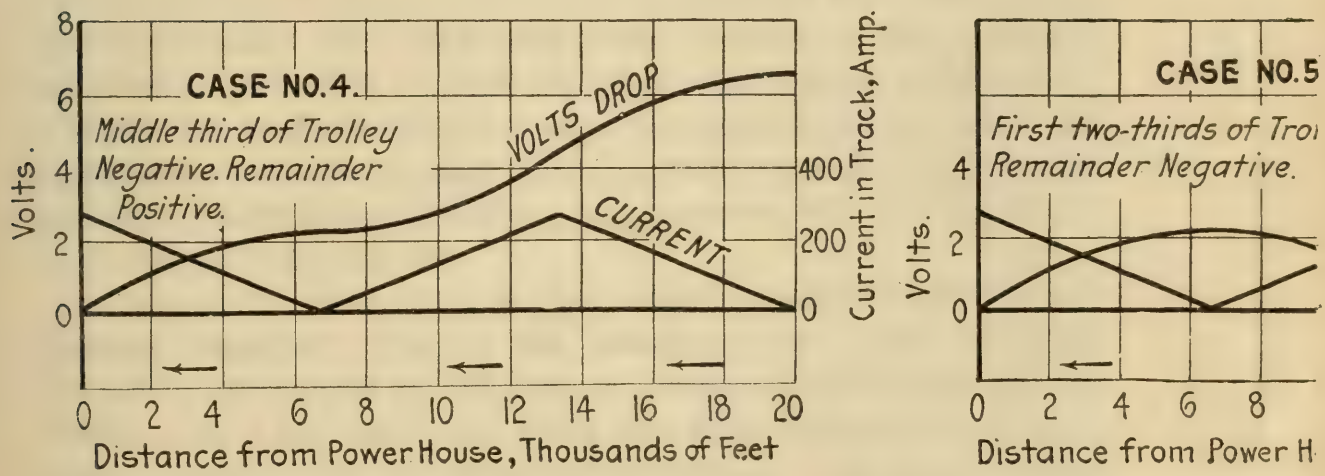

CASE NO.3.
First 0.707 of Trolley Positive,
Remainder Negative.
VOLTS DROP
CURRENT
Volts
4
2
0
400
200
Current in Track, Amp
0 2 4 6 8 10 12 14 16 18 20
Distance from Power House, Thousands of Feet


ley Positive,
CURRENT
VOLTS
DROP
400
200
0
Current in Track, Amp.
10 12 14 16 18 20
ouse, Thousands of Feet


CASE NO.6.
Middle half of Trolley Positive,
Remainder Negative.
VOLTS DROP
CURRENT
Volts.
4
2
0
200
0
Current in Track, Amp.
0 2 4 6 8 10 12 14 16 18 20
Distance from Power House, Thousands of Feet.

.6





66325°—18. (To face page 105.)

FIG. 3

track, assumed to be uniformly applied. This is equivalent to a headway of betwen three and four minutes each way.

Case 1 is that of normal operation with the trolley all positive. It is seen that the current on the track increases uniformly from zero at the end of the track to 800 amperes at the power house. This corresponds to a maximum gradient at the power house of 2 volts per 1000 feet. The voltage curve showing the drop in voltage from any point on the track to the power house is obtained by integrating the IR drop over the entire length of the track, its equation being that of a parabola. The total drop is seen to be 20 volts.

In case 2 the first half of the trolley is supplied with current from a negative generator, and the outer half from a positive generator, a 1200-volt trolley breaker being required between the two sections. Under this arrangement the outer half of the track is uniformly collecting current, while from the first half the current is being uniformly withdrawn through the cars and returned to the power house over the negative feeder. The cars on one-half of the track are, therefore, in series with those on the other half, and no current is returned to the power house over the track or neutral conductor. In the practical application of this arrangement, as the cars move back and forth across the section breaker, there will be an unbalanced portion of the load at times which must return to the station or be supplied from the station over the track. The maximum track current, track gradient, and over-all potential are here only one-half as great as in case 1.

Where the traffic is frequent, as on city streets, the unbalancing is not serious and the average currents and potentials, which really determine electrolysis conditions, are not essentially different from those shown in the curves.

In case 3, the first 0.707 of the trolley is positive and the remainder negative. This is the condition for a zero over-all potential. As shown by the arrows, there is an outward flow of current over a portion of the track and both extremities are at a lower potential than the intermediate region. The effect of this is to produce two positive areas in the underground piping systems and to require drainage of telephone and power cables at two points instead of one. Such a condition might be taken care of satisfactorily, were it not for the fact that the shifting loads

which occur in practice cause the potential of the outer end of the track to fluctuate through rather wide limits. By shifting the trolley section breaker from the 0.707 position to the two-thirds position, as shown in case 5, the potential of the outer end of the track falls to more than two volts below that at the power house. A slight shift of the breaker in the opposite direction would raise its potential correspondingly. It follows, therefore, that if pipes or cables are drained to the outer end of the track, as well as at the power house, under conditions similar to those shown in cases 3 or 5, a shifting of the load will result in a fluctuation of the potential between these two points and an unnecessary transfer of current over the drained structures.

This objection is overcome in case 4 where the middle third of the trolley is negative and the remainder positive. It will be seen that here the gradient is continuous from the outer end of the track toward the power house, although at one point it drops to zero. The maximum track current and over-all potential are reduced to one-third of the corresponding values of case 1. Unless considerably more than one-third of the load be reversed, there is no danger of getting two low-potential points on the track as occur in cases 3 and 5.

Another arrangement of trolley sections is shown in case 6, where the middle half of the trolley is positive and the two end sections negative. The track currents and gradients are here limited to low values, but the same objection is encountered as in cases 3 and 5.

In locations where the outer end of the track extends into an undeveloped territory, with no underground structures present, this objection is not pertinent, and the arrangements shown in cases 3, 4, and 6 may be employed with no bad consequences. The actual arrangement of the trolley sections in any particular instance where a two-wire system is being converted for three-wire operation will, of course, depend very largely upon the existing arrangement of the feeders. It will usually be desirable to employ these with as few changes and additions as possible, and they may easily prove to be the determining factors in the sectionalization of any system.

(*e*) *Insulation of Trolley Sections.*—The problem of insulating the positive and negative trolley sections from each other is one

that will require considerable care. At points of simple juncture this has been accomplished in some cities by the use of two standard 600-volt trolley breakers in series, with a dead section of trolley wire from 4 to 6 feet in length between them. Unless the dead section between the two live trolley wires is of considerable length there is danger of drawing an arc across the span upon the passage of a car. Where trolley wires of opposite polarity cross it will probably be found better to make the entire intersection of one polarity rather than try to insulate the crossings. At the intersection of two double-track lines this will mean the installation of four double breakers as just described. Where such changes are made, the more important of the two lines should be made the continuous one to avoid interruption of service due to failure of power on the other line.

Warning signs should be hung on the span wire at all breakers and motormen should be instructed to coast across these points. Failure to do so will ordinarily result in no particular harm, but as the voltage of the two trolleys may at times be quite different, it is a matter of safety to do so.

As trolley feeders are already insulated for 600 volts against ground, no increased insulation on pole lines or underground feeders will be found necessary. However, where the two polarities are carried on the same pole, workmen will have to exercise care when working on the lines. It may be found desirable to tag, or otherwise mark, the two sets of feeders where they are in conflict and in some cases it may even be necessary to shift some feeders to avoid dangerous conditions.

(*f*) *Switchboard Changes.*—The amount of labor and material necessary to convert the switchboards of existing installations for three-wire operation will depend upon the degree of flexibility desired. The most ideal arrangement from the operating standpoint would be a double bus construction throughout with double-throw switches on all feeder and machine panels. This would permit of operating any or all generators on either the positive or negative bus and of throwing any feeder, at will, to either bus. Such an arrangement would, however, require radical changes in many stations, amounting practically to a reconstruction of the switchboard, and this, for the slight advantage of increased flexibility would not in general be warranted.

Where switchboards are not already provided with double busses and double-throw switches, it will be necessary to provide some of the generators with double-throw switches or some other means of supplying an auxiliary feeder bus with negative current. The feeders selected for reversed polarity can either be provided with double-throw switches or in lieu of these, an additional panel can be employed for each feeder to energize it from the negative bus. Several arrangements are possible and the one to be selected will depend entirely upon local conditions and requirements. It will usually be necessary to either install interlocking switches to prevent closing a switch on a 1200-volt short circuit, or to formulate strict operating rules to guard against such an occurrence.

(*g*) *Conversion and Operating Costs.*—The three-wire system has sometimes been considered as a means of increasing the economy of power distribution. While it does accomplish something in this direction, it does not possess the advantage that is at times claimed for it. A little consideration will show that a perfectly balanced three-wire system operating with 600 volts on each side is identical with a 1200-volt, double-trolley system in so far as the amount of feeder copper required is concerned. Since in any double-trolley system the amount of copper required on the return portion of the circuit would be, in general, equal to that on the outgoing lines, the total copper for a 1200-volt, double-trolley system would be substantially the same that is required for a positive feeder system of a 600-volt, track-return system. It follows, therefore, that a three-wire system requires the same amount of copper and the same energy loss in the feeders when we consider both positive and negative sides as is required in the positive-feeder system of the ordinary 600-volt network.

The only economy resulting from the installation of the three-wire system, therefore, is the saving in track losses, which are greatly reduced, although not entirely eliminated. Track losses however, are generally much smaller than the losses in the positive-feeder systems, so that the economy in this feature, while important in some cases, would be very small compared with the economy that would result from doubling the voltage on the ordinary track-return system.

The relatively small saving in the track losses are, however, largely offset, if not more than counterbalanced by the increased station losses due to necessity of always maintaining two sets of generators. The cost of converting a system for three-wire operation is small if compared to the cost of a negative insulated feeder system or additional substations that would give the same degree of protection from electrolysis. Where, as in many cities, uninsulated negative copper has been installed, this can be reclaimed after conversion to three-wire operation, and will go a long way toward, if not entirely cover, the cost of the conversion.

12. NUMBER AND LOCATION OF POWER HOUSES AND SUBSTATIONS

In a general way the effect of the number of feeding points on the potential drops in the rails and the consequent leakage of current from the tracks is obvious, but some of the more important aspects of this problem are obscure and often not appreciated. The economic aspect of the question is also more complex than is generally recognized. In the broadest terms we may consider the matter under two heads, namely, (1) the effect of the number and location of the stations on the tendency of the pipe systems to pick up stray currents from the return, and (2) the effect on the total drop of potential on both sides of the line.

As to the first of these we have to consider the fact that as the number of stations is reduced the capacity of each must be increased, with the result that the current flow in the rails approaching the power house will be greater and the increased potential gradients resulting therefrom cause correspondingly increased leakage of current from the tracks. Further, as the distance between stations is increased the tendency of pipe lines to take up current from the earth under a given potential gradient increases much more rapidly than the distance of transmission. In fact, it can be shown that the current picked up by the pipes may increase either as the second, the third, or even a higher power of the distance between feeding points, according to the character of the system under consideration. Any increase in the number of feeding points, or, more properly speaking, the number of "drainage points" or points at which current is taken from the track, will reduce in much greater degree the flow of stray currents in the pipes.

The number of drainage points can be increased to any desired extent by the proper use of insulated negative feeders, as above described, but the fewer the stations the longer and heavier the feeders must be, and in consequence of this an increase in the number of stations may often prove to be in the interest of economy, considering only the negative return. This economy will become much more pronounced when we consider also the distribution of the power on the positive side as well as its return on the negative.

When we come to consider the question of total drop of potential in the distribution and return of the current we have many complex factors to consider. One of these factors is the loss of power resulting from such drop of potential, but the calculation of the value of this lost power is by no means so simple as might at first appear. It is not sufficient simply to determine the total energy loss during any given time and multiply this by the cost of power per kilowatt hour in order to determine its value. We must consider that the loss of power is proportional to the square of the load and hence is greatest at time of peak load when the capacity of the power station is usually taxed to its utmost. The capacity of the generating plant and hence the fixed charges on the cost of power are thereby increased; or if the power be purchased, there is usually a fixed charge imposed on the maximum demand. In any case if the operation of the system is such that the line losses give rise to an increased demand for power at time of peak load, the cost of the lost power will be greater than the cost of the power utilized at the cars.

Besides the question of lost power due to line drop we have to consider also the effect of this drop of potential on the character of the car service and the cost of operation of the car system. Low voltage means lower average car speed, with a consequent increase in the number of cars required to operate at a given headway, which in turn increases both fixed charges and operating costs. Any change in the distribution system, therefore, whether a change in the number of stations or any other change which affects materially the line losses, will exert a marked effect on the cost of operation of the system. In designing a system of electrolysis mitigation, therefore, many things have to be taken into account quite apart from the technical points regard-

ing the electrical condition of the negative return, if a proper balance is to be maintained between the cost of making the proposed changes and the benefits resulting therefrom.

In considering the installation of a new system of electric power distribution for street railways complete, without regard to existing power stations, it would be a comparatively simple matter from a detailed study of the system in question to determine the proper number of stations and the best location of the same in order that best results might be secured, all things considered. But even if such a system were installed which answered in an ideal manner the requirements of present-day service, it would be but a few years until the growth of traffic and shifting of business centers would require increases in the size of the plants and other changes which would make the system much less economical than the ideal.

In studying a system already installed we may be able to show that the feeding distances for some or all of the various stations are too great for economy and that a greater number of stations with reduced feeding distances would provide a much more economical system of distribution. It does not follow, however, that an increase in the number of stations in such a system will actually improve its economy, but on the contrary the reverse might be the case, for, although the present feeding distances may be considerably too great for maximum economy, the location of the stations with respect to each other may be such that the placing of a new station in between will overstep the point of most economical feeding distance and even raise the net cost of operation, whereas the cost of moving old stations to more desirable locations might be altogether prohibitive.

In dealing with existing conditions, therefore, we must work under considerable restriction, and many things must be taken into account before it can be determined definitely whether or not a proposed substation will prove desirable from an engineering and economic standpoint.

Automatic rotary converter substations have now been developed to the point where they are entirely practicable and dependable for railway use, and the saving in operating expense which can be affected by them is very encouraging to the street railway companies. The machines automatically start up when

the trolley voltage reaches a selected minimum value and carry the load until it reaches a certain sustained minimum value when it is automatically disconnected from the circuits and shut down. No regular attendant is required but frequent inspections are of course important.

So far, these stations have been used chiefly on interurban lines, where the saving in energy is an important factor as well as reduced operating costs. Some installations, however, have been made for city service where the machines run continuously for 18 hours each day, or through the morning and evening peaks. The extra investment necessary for the automatic control feature is relatively small, and it is believed that this new development will materially increase the number of feeding points which can economically be provided for any large street railway system and, incidentally, thereby give better electrolysis conditions.

13. SUMMARY OF METHODS OF MITIGATION

In the foregoing review of the various methods that have been proposed for reducing troubles from electrolysis those treated in the first section relate solely to protective measures to be applied to the pipes. Of these the first seven are found to be of little value for extensive application to networks of any considerable size, and certain of them are shown to be actually detrimental because of their tendency to accelerate deterioration of the pipes. The method of insulating joints, and a properly designed pipe drainage system are of practical value, but it is recommended that their use be restricted to auxiliary measures used in connection with certain of the measures described in the second section for application to the track return system. This recommendation is made for two reasons—first, because the practical working out of these systems applied to the pipes usually places an undue part of the burden of mitigation on the pipe owning companies, and second, because the adequate protection of all subsurface structures by either of these means in cities where potential gradients are allowed to remain high will in general prove a difficult and expensive matter.

A more logical and at the same time a more effective and often more economical procedure is to attack the source of the trouble by eliminating in a large measure the leakage of the electric

currents into the earth. Numerous methods applicable to the railway return system are available for this purpose, but, as pointed out in the foregoing review, the majority of these, namely, the alternating current system, the double trolley system, the use of negative trolley, the periodic reversal of trolley polarity, and the use of uninsulated negative feeders in parallel with the rails, when considered solely as methods of electrolysis mitigation, are either impracticable or else open to the objection that the expense or operating difficulties attending their application are rendered unnecessary because of the fact that there are other adequate methods available for general application which are comparatively cheap to install and which introduce but slight complications into the operation of the system.

The importance of proper construction and maintenance of track return is emphasized. Thorough bonding and cross bonding are urged, and it is pointed out that at times it may be desirable on the ground of economy to use somewhat heavier rails than would be called for solely by traffic conditions. The drainage of roadbed where practicable is also urged, and where track is laid on private right of way the rails and ties should be kept, as far as possible, out of direct contact with the earth in order to reduce leakage of the current to a minimum. Good well-drained rock ballast is very effective for this purpose.

It is also pointed out in the foregoing that a three-wire system, when viewed solely from the standpoint of electrolysis mitigation, possesses large possibilities, and experiments with these systems under favorable conditions are urged. Attention is called to the fact, however, that up to the present time sufficient experience has not been had with these systems to show whether they are practicable from the operating standpoint under average conditions of service. At the present time it must be regarded as an experimental system which may under favorable circumstances be found of value in relieving electrolysis troubles.

The most effective methods that have been thoroughly tried out in practice over long periods are the use of insulated negative feeders, either with or without boosters, as described above. It is pointed out that in most cases where the feeding distances are not too long an insulated feeder system without boosters will

prove cheapest and at the same time more satisfactory because of its greater simplicity. It is possible by the proper application of either of these insulated feeder systems to reduce the potential gradients in the earth to such low values that in most cases little damage would result, and they can consequently be made very effective in relieving electrolysis trouble.

In many cases, however, it may be better where conditions are favorable to combine one of these methods with either the insertion of a moderate number of insulating joints in the pipes or with the use of a very limited amount of pipe drainage, providing conditions are favorable to its use. The insulated-feeder system would be applied to reduce the potential gradients throughout the system to very low values and one or the other of the auxiliary systems used to eliminate largely any residual electrolysis that might still remain.

By the proper use of the measures set forth above it is in most cases possible to secure sufficiently low-voltage drops in the negative return to afford adequate protection to underground pipes, so that there will be little need for resorting to the use of any auxiliary measures, such as pipe drainage or insulated joints in the pipes. In fact, it has frequently been found that a careful study of the power distribution system, such as should always be made in connection with the design of an electrolysis mitigative system, will show that changes in the distribution system could be made that would yield operating economies which quite apart from any considerations of electrolysis protection are more than sufficient to justify the expense involved. We have found this to be true in so many cases that we are convinced that the adoption by the railway companies of the best measures for reducing voltage drops to such low values as substantially to eliminate electrolysis trouble would in very few cases result in financial hardship.

V. REGULATIONS REGARDING ELECTROLYSIS MITIGATION

1. NEED FOR REGULATIONS

The many conflicting interests involved in the electrolysis problem make it imperative that some sort of regulations governing the procedure of the various parties in interest be adopted if

a permanent and just settlement of the problem is to be secured. It is true that conditions vary greatly in different localities, and always to attain a complete solution would require a separate investigation for each case. In general, however, it is not practicable to make a detailed engineering investigation of each locality, such as would be necessary in order to prescribe regulations especially adapted thereto. As in all other cases where diverse interests come into conflict the interests of all will be best safeguarded by the adoption by a proper authority of more or less specific regulations defining the responsibilities, rights, and limitations of the parties to the dispute.

In the case of electrolysis, long experience both in America and abroad has shown that some sort of regulations are necessary for protecting underground pipes and cables and that such regulations can be made very effective. To be sure, any set of regulations drawn to meet average conditions might in special cases fail to give sufficient protection, and in other cases might cause somewhat greater expense than would be necessary if each case could be considered in detail by itself. Such regulations would, however, insure fair and adequate treatment of all parties concerned under general average conditions, which would be a great improvement upon present practice in most places. Such regulations wisely drawn would not alone protect pipe-owning companies, but would often benefit the railway companies also. In the absence of such regulations a single serious case of trouble traceable to electrolysis such as might occur, or the activity of interested or overenthusiastic individuals, may lead to hasty and ill-considered legislation, resulting in rules much more drastic than conditions call for, and lead either to undue hardship on the railway companies or to long and costly and perhaps fruitless litigation.

Regulations would also define definitely what is expected of the railway companies and enable them to treat the matter as one of the definite engineering problems connected with the operation of the railway system. They could thus plan and build definitely and with the assurance that they would not be continually harassed by agitation of the subject of electrolysis.

2. PROPER AGENTS FOR DRAWING PROPOSED REGULATIONS

It is very important, however, that such regulations should be drawn with the greatest care and with due consideration of the interests both of the railway and the pipe-owning companies. They should not be drawn by persons unfamiliar with requirements, nor by the representatives of any one of the interests concerned, but by all of such interests acting jointly. It is hoped that such joint action may be taken in the near future as a result of the work of the American Committee on Electrolysis [8] now at work on the general subject of electrolysis. The work of that committee is primarily educational and is not concerned at all with the legal aspect of the question. Nevertheless, a careful scientific and engineering study and report will lead at least to a partial definition of the requirements and responsibilities of the various utilities interested in this problem.

3. PRINCIPLES ON WHICH REGULATIONS SHOULD BE BASED

It is not our purpose to present here anything in the way of a set of regulations suitable for enactment into law. We shall, however, discuss briefly the fundamental principles on which we believe such regulations should be based.

The various factors which determine the electrolytic conditions of underground structures, such as overall potentials and potential gradients in the track or pipe network, potential differences between pipes and tracks, and between various pipe and cable systems and the earth, current flow in the pipes, current density of discharge from the surface of pipes, etc., while important in any complete electrolysis survey, are for the most part subject to such a variety of influences that they are not suitable for use as a basis for regulations. The factors selected must not only afford a fair criterion of the general electrolysis situation, but they must at the same time be susceptible of easy measurement, and they must lend themselves to ready and fairly accurate predetermination, so that the railway return system can be designed to meet the regulations with a minimum of uncertainty.

All of the above-mentioned factors except the overall potential measurements, and potential gradients in the track return, are affected to a great extent by the character of the pipe systems,

[8] The work of this committee has been discontinued for the period of the war.

and changes in the latter may produce marked changes in most of the former; and hence these factors are only partially under the control of the railway company. Further, none of these other factors except the potential drops on the pipe systems afford an accurate criterion of the danger from electrolysis. They are therefore unsuitable for use as a basis of specific regulations designed to protect underground structures.

The overall potential and potential gradient measurements, on the other hand, particularly those taken on the pipe systems, afford practically as good a criterion of the danger existing when interpreted in the light of general experience as any other measurable factors. They are fairly definite, readily measurable, and in very large degree under the control of the railway company; hence they are best adapted for use as a basis of rules and regulations.

In all laws and regulations that have up to the present time been adopted, so far as we are aware, the over-all potentials and potential gradients have been specified as those taken between various points on the railway tracks. This is true of the various European ordinances as well as those adopted in this country. These are very good criterions in many respects and have proven successful, particularly in Europe, in relieving electrolysis troubles. There is much to be said, however, in favor of limiting potential drops on the earth or on pipe networks rather than on the railway track. Such voltages afford the most accurate criterion of all, as to the actual danger to the underground structures, and would also prove more advantageous to the railway companies.

If potential drops on the earth or pipes be made the subject of limitation, higher voltages could be allowed in those tracks having a high resistance to earth. This would apply to tracks laid on a well-drained roadbed, for example, and with still greater force to tracks on private right of way where the rails are set up on ties out of contact with the earth. On the other hand, relatively low voltages would have to be maintained in tracks in which the rails are much of the time in intimate contact with moist earth, or otherwise constructed so as to give a comparatively low resistance to ground. Under this plan low voltages in the track would be required only where most needed and the railway company would be encouraged to so construct the tracks as to give a high leakage

resistance to ground. It is evident that if the leakage resistance to ground be made high, practically all of the current will be compelled to return to the negative bus by way of the railway negative return and thus increase the voltage drop on the tracks, although reducing electrolysis troubles. If, however, the voltage drop on the tracks is limited by regulations any construction of roadbed that would reduce leakage would increase the difficulty and cost of complying with the regulations. On the other hand, if the voltage drop on the pipes is made the basis of the regulations, the railway companies would profit by any construction which tends to reduce leakage instead of suffering by it, as in the case where voltage drops in the tracks are limited. If this plan were adopted, it would of course be necessary to prescribe lower voltage limits than would be applicable to tracks in order to secure the same freedom from electrolysis.

4. VOLTAGE LIMITS IN TRACKS

(*a*) *Previous Experience Regarding Voltage Limitations.*—In this country little experience has been had until recently with railway installation in which voltage drops in the negative return have been maintained low enough to give substantial freedom from electrolysis trouble. The prevailing practice in a majority of the cities of America has been to permit rather high voltage drops in the return circuit, and it is for this reason mainly that electrolysis troubles have assumed much more serious proportions in this country during the past decade than in almost any other country. There has, therefore, been but little experience in this country that can be used as a reliable guide as to just what voltage limits can be considered safe, although there is abundant and incontrovertible evidence in regard to what voltage limits may, under many circumstances at least, be considered unsafe.

On the other hand, in Great Britain and many parts of continental Europe much experience has been had with installations in which quite low voltages have been maintained over a period of many years; and this long experience has shown that the voltages which have been maintained in these countries are such as to insure, under average conditions, substantial freedom from electrolysis. This experience, therefore, is a valuable guide in

determining what voltage limits can be considered safe under similar conditions here.

(*b*) *Voltage Limits Prevailing in Great Britain.*—In Great Britain the maximum allowable voltage drop between any two points of any railway system, near which underground metallic structures are laid, is limited by law to 7 volts. This law has generally been complied with by the railway systems of Great Britain, and where this 7-volt limit has been substantially complied with there has been comparatively little trouble from electrolysis of underground structures.

In some instances this legal limit has been considerably exceeded, due primarily to the fact that the British Board of Trade, which is charged with the responsibility of administering the law, has not made it a practice to make investigations of electrolysis conditions on its own initiative, but only on the complaint of interested parties. For this reason isolated cases can be found in which the prescribed voltage limits are for a time exceeded, and it is doubtless due largely to this fact that most of the electrolysis trouble, that has been experienced in Great Britain, has occurred. On the other hand, in many cities in Great Britain the limits prescribed by the ordinance have not only been met, but the prevailing voltage drops under ordinary traffic conditions have been found to be considerably below the maximum limit prescribed by law.

The accumulated experience with the voltage limits which prevail in Great Britain appears to show quite conclusively that voltages of the order of the magnitude of those maintained in the railway systems there are none too low to assure adequate protection to underground structures; and it is the opinion of some competent engineers that even lower limits are desirable and commercially practicable. This attitude was taken by the engineers who drew the regulations that are now in effect in many cities of continental Europe.

(*c*) *Voltage Limitations in Germany.*—The so-called German regulations, which are in effect in many cities in continental Europe, while differing radically in the manner in which the voltage limits are defined, were designed by the framers of the regulations to yield somewhat lower average voltage conditions

than those demanded by the British law. The German regulations prescribe a voltage limit of 2½ volts throughout any city network of street railway lines, and they further prescribe a limit of 1 volt per kilometer (0.3 volt per 1000 feet) on interurban lines. These limits are applied to the period of average scheduled traffic instead of to the peak-load period, as in the case of the British law.

In both of these sets of regulations, the definition of voltage limits is indefinite and unsatisfactory. The British law limits the maximum drop to 7 volts, but does not specify whether it is the momentary maximum that is subject to limitation, or the sustained maximum during some definite interval of time. In applying the law, however, the British Board of Trade has found it necessary to adopt for administrative purposes a more specific definition of the term "maximum voltage." In determining this maximum voltage, the average value for the half hour of highest load is determined, and also the maximum momentary drop during this period, and the mean of these two values is taken as the maximum voltage within the meaning of the law.

In the German regulations a similar ambiguity exists. While it is stated that the voltage under average scheduled traffic should not exceed certain values, it is debatable whether or not it is intended that the momentary value of voltage drop under ordinary schedule traffic is to be kept within the prescribed limit or whether the average value of voltage drop under normal operating conditions is the value to be considered. If we place the latter interpretation on the question, the limit appears to be reasonable and practicable, and one that would, under many circumstances, be applicable in this country. If, however, it is intended to limit the momentary voltage under average load conditions in street railway networks to 2½ volts, the regulation would be altogether too severe for general application, as a voltage limitation of this severity is not needed for providing reasonable protection to underground pipes and the cost of meeting such limitations would be altogether out of proportion to the benefits that would accrue therefrom.

If we assume, then, that this over-all voltage limit of 2½ volts is to be taken as the average value under normal scheduled traffic, it would be found to compare very well, so far as ultimate results

are concerned, with the voltage limits in effect in Great Britain. It will be apparent that the maximum value of 7 volts, defined as the mean value between the average for the maximum half hour and the highest momentary value for that hour would correspond to a mean value for the maximum half hour of approximately 4 to 6 volts under most traffic conditions. On a basis of 50 per cent load factor, this would give a mean value under average load conditions of 2 to 3 volts, which is of the same order as the 2½ volts average limit named in the German regulations.

The above discussion relates only to the over-all voltage limits prescribed by the regulations in question. The German regulations make no provision for restricting the potential gradient within the city network proper, the gradient limits of these regulations applying only to interurban lines. The British law, however, contains a provision which limits the current density in any street railway rail to 9 amperes per square inch of cross section. This, in effect, prescribes a potential gradient limit, which, however, is variable according to the resistivity of the rails; and for rails of average resistivity this gradient limit would yield a maximum potential gradient of approximately 0.9 volt per 1000 feet, exclusive of the drop on the joints. This would correspond to an average all-day gradient of from 0.3 to 0.4 volt in the case of most railway loads.

It is very desirable to have both the overall voltage limit and the potential gradient limit, the latter to prevent too rapid change in the potential of the tracks in any locality, which makes it difficult to prevent large potential differences between pipes and rails from developing locally, and the former to prevent the use of excessively long feeding distance, which, even with a small gradient, would permit the accumulation of large potential differences between pipes and tracks.

(*d*) *Manner of Specifying Voltage Limits.*—As to the manner of specifying the limiting voltages that should be allowed, there is a good deal of difference of opinion. Some prefer to specify a limit for momentary voltages, and others advocate restricting the maximum value for some definite short period, such as 10 to 30 minutes during the peak-load period, while many prefer to follow the practice of specifying an upper limit for the average voltage during the

operating period. We have become convinced that the last plan is in general to be preferred.

Our investigations have shown that the actual amount of corrosion which takes place is much more nearly proportional to the average all-day load than it is to any short-time peak value. In fact, investigations made at the Bureau of Standards,[9] show that as the load increases and the current density is thereby increased the actual amount of corrosion does not increase as fast as the current increases. For this reason it is undesirable to place a heavy penalty on a high peak of short duration, provided the average current is small. This objection is avoided entirely by specifying the average value of the voltage instead of some short time peak-load value.

To specify a limiting value of voltage during from 10 to 30 minutes would probably not be a serious matter in the case of a congested city district, where the railway loads are comparatively steady and the load curve shows a comparatively flat maximum. In case of suburban or interurban lines operating an infrequent schedule, particularly where multiple car passenger trains and heavy freight trains are operated, any short-time voltage limitations will almost always impose upon the railway company a hardship that is altogether out of proportion to the benefits that could possibly result from such a method of defining the maximum.

In the case of interurban railway systems, any voltage limitations based upon momentary maximum values would be practically prohibitive, unless the voltage limit were placed so high as to be of no real value for general adoption. It seems best, therefore, that any voltage limitations that may be applied be based upon the all-day average value of the voltage rather than on any short-time period. Investigations have shown that if the polarity of the pipes reverses frequently, as, for example, every few minutes or oftener, the actual amount of corrosion which results is practically proportional to the algebraic average value of current due to the fact that for short periods of reversal the corrosive process is in large degree reversible. If, however, the frequency of reversal is very low, the reversal taking place once an hour, or at longer

[9] Burton McCollum and K. H. Logan, "Electrolytic corrosion of iron in soils," Bureau of Standards Technologic Paper No. 25.

intervals, the corrosion increases and tends to become more nearly proportional to the average value of current during the time when the pipe is positive to earth, the average being of course reduced to a 24-hour basis.

Owing to the uncertainty of the length of the periods of reversal that may occur under average operating conditions, it is best in fixing voltage limits in practice to base the limiting values on the 24-hour average value of voltage during those periods when the pipe frequently becomes positive to earth. In interpreting the significance of voltage readings actually taken, however, where the frequency of reversal is always approximately known, it is best to bear in mind that for periods of reversal of a few minutes or less the algebraic average affords a better criterion of the damage that will result than the arithmetical average.

A careful study of the local conditions in this country, in the light of the extended experience in European countries with the voltage limits that have prevailed there for many years, indicates that the average all-day voltage drop in the railway tracks under average conditions should be restricted to a value not exceeding about 2 to 4 volts, the lower value applying to localities such as business centers in large cities where the underground utilities are highly developed and of great value, and the higher value to those regions in which the utilities are developed to a lesser extent, such as the average residential districts in cities.

In very sparsely settled districts still higher voltage drops may be permitted, and in many cases, especially where tracks are on private right of way and substantially insulated from earth, thoughout their entire length the voltage limits may even be dispensed with altogether. Thus, in fixing regulations for any given city, some sort of a zone system is desirable, different voltage limits being prescribed for different zones, according to the value of the underground utilities and other local factors.

These all-day average values of 2 to 4 volts would, in the case of the majority of railway loads, correspond to an average during the maximum hour of from 3 to 10 volts, there being a greater variation in the values for the shorter than for the longer period. The average gradient corresponding to this over-all limit will

depend in large measure on the means that are adopted for complying with the limitation and on the feeding distance. A study of the best methods available for reducing voltage drops indicates that the average 24-hour gradient at any point in the rail should under average conditions not be permitted to exceed about 0.3 to 0.4 volt per 1000 feet.

These limits of 0.3 to 0.4 volt per 1000 feet for the 24-hour period correspond roughly to 0.4 to 0.5 volt per 1000 feet for the 18-hour operating period. If the drop of potential on pipes or earth is made the basis of limitation, lower values would have to be used. Experience indicates that, on the average, over-all potentials and potential gradients in the earth should be maintained at about one-half the figures given above in order to insure the same freedom from electrolysis.

We do not wish to be understood as taking the view that the average voltage for the maximum hour or even half hour can not be made a satisfactory basis for voltage regulation. Experience has shown that either plan can be made to work out very well in practice. Recent investigations, however, show that the use of the longer period is a more rational basis of fixing voltage limits, since it gives a factor which is more nearly proportional to the actual danger involved than any other. Cases continually arise in the operation of street railway systems where local traffic congestion will cause very excessive voltage drops locally for short periods of from 5 to 15 minutes or longer, but these occur so infrequently that they have but slight effect on the average all-day values, and hence on the total damage from stray currents.

To adopt any rule which would limit these transient rises of voltage to very low values would involve an expense to the railway company which would be out of all proportion to the benefits that would accrue to the owners of underground utilities. On the other hand, if the voltage limit is placed high enough so that it can reasonably be applied to lines having very heavy transient loads, it would be altogether too high for other lines having comparatively steady loads. If the all-day average value is used, however, the cost of meeting the limit, as well as the degree of protection, will be independent of the character of the load on different lines.

As to the convenience of determination of the voltage limits prescribed there is little to choose between the two plans. Even if a short period be adopted, it will be necessary to use recording voltmeters, and records would have to be taken over practically the entire day to make sure that the limiting values were being recorded, and when the all-day record is at hand, the all-day average value can be obtained with practically the same facility as the average for shorter periods. The all-day average value of voltage would therefore appear to be the most natural and logical criterion to use as the basis of voltage regulations. Whatever method may be ultimately adopted for defining any maximum allowable limits that are to be prescribed for any particular locality, extended experience both in this and in foreign countries shows that the average values must not greatly exceed the figures mentioned, provided reasonable and permanent protection is to be accorded to the underground pipe system.

5. GENERAL SCOPE OF REGULATIONS

(*a*) *Voltage Limitations.*—From the foregoing it will appear that one of the most essential things to be incorporated in electrolysis regulations is an appropriate limitation of the potential drops in the railway track network, or in the earth and pipe systems, and that such limits should be applied in the case of railway tracks to both the over-all potential drops between remote parts of the system and also to potential gradients in relatively short portions of the track network, the former being necessary to guard against the accumulation of large potential differences which might occur even with low gradients, provided the feeding distances are very long, and the latter to prevent the very rapid change in the voltage of the track in any portion of the system which might give rise to bad local conditions even though the over-all potentials were kept comparatively small.

In fixing voltage limits for regulation it is desirable to specify the manner in which the voltages are measured and potential drops computed. In determining the potential gradients the voltage drop on a distance of 1000 feet is generally better than a much shorter length. This length is long enough to give a fair average condition over a considerable length of track, and at the

same time short enough to prevent any serious accumulation of potential difference at any point, provided the limits mentioned above are substantially complied with. In calculating the potential gradient it is best to measure the distance in an air line between the terminal points, provided the region crossed by this line is occupied by pipe networks; but if the pipe networks follow an indirect course, measurements should be made by way of the pipes.

(*b*) *Potential Wires.*—In order to facilitate the determination at any time of the voltage drop, it is very important that permanent potential wires be installed running from a suitable terminal board at some central point and connected to the tracks or pipes at those points between which potential measurements are to be made. These should always be run to the more outlying points and also to the point in the system of approximately lowest potential so that the maximum over-all potential drops can be directly measured. It is desirable also in most cases to have some wires run to intermediate points, so that any high potential drop that may be observed can be approximately localized by measurements with the potential wires. Such wires may either be especially installed for the purpose of taking potential measurements, or wires for this purpose may be leased from a telephone company. When satisfactory terms can be arranged, the leasing of wires is preferable, since the maintenance of these wires would, in general, be less than of special wires run separately for this purpose.

In view of the fact that the purpose of the potential wires is not primarily for the protection of the pipe systems but rather to supply information to all parties concerned as to the conditions which exist, it seems preferable that the expense of installing and maintaining or of leasing such potential wires should be borne jointly by all of the utility companies directly concerned in the electrolysis mitigation problem. If this were done, the cost to any particular company would be practically negligible and it would remove any material objection which the railway company might otherwise have to the installation of such potential wires. Graphic voltmeters should also be provided for measuring and recording the potential differences required.

(*c*) *Connections Between Tracks and Pipes.*—Metallic connections between underground metallic structures and the street railway tracks should never be permitted at any point where the pipes might become negative to the tracks and such ties deliver current into the pipe system. Such connections are sometimes advocated as a means of reducing voltage drops in the negative return, but the objections to such procedure are too obvious to be discussed here. It is not desirable in general to prohibit all metallic connections between pipes and railway negative return in the regions near the power stations, although in general in city systems such connections are not desirable, except in the case of lead cable systems where properly restricted drainage may be used. There are, however, special cases in which it might be desirable to install such ties on pipe systems, and this should not be entirely prohibited by the regulations.

(*d*) *Interconnection of Tracks.*—Wherever two or more railway systems operate in the same territory it is of the greatest importance that the tracks should be electrically connected together at all intersections and such interconnection should be required by regulations. In special cases where tracks, either of the same or different railway lines, parallel each other for a considerable distance, such as half a mile or more, and where the tracks are only a block or so apart, it is important that occasional crossties between the lines be installed to prevent wide fluctuations of voltage between them. This would be a special provision designed to meet local conditions rather than a general rule.

(*e*) *Track Maintenance.*—If the voltage drops in the tracks be limited by regulation and if a sufficient number of potential wires are installed not only to the remote points of the system, but also to intermediate points so that the potential gradients on practically all sections of the track of lengths from 1000 to 3000 feet can be readily measured, it would not appear desirable to superpose on this any additional regulation in regard to track maintenance, leaving that matter entirely to the railway company. If, however, potential wires are connected only to the remote portions of the network, they would not give sufficient data in regard to electrolysis conditions at intermediate points, and in such cases it would be desirable to have some sort of regulation covering track

maintenance. This might take the form of a rule requiring periodic tests and reports of the condition of the track bonding, and definitions regarding what may be considered a good or bad bond.

Practice in regard to the latter point varies considerably in this country, but in general where the resistance of a joint (including 3 feet of rail) exceeds the resistance of a length of from 6 to 10 feet of rail the joint is considered defective. Cross bonding between tracks should also be required at frequent intervals.

The best practice in this country at the present time calls for cross bonds at intervals of from 200 to 500 feet of track, according to traffic conditions, and bonding at shorter distances is required where the traffic is heaviest. Such bonds should be designed to carry the maximum current to which they can be subjected in use.

(*f*) *Exemptions.*—Where railway lines operate in a territory remote from pipe systems exemptions from stringent regulations should generally be made. The German regulations exempt entirely railway lines which operate at a distance exceeding 200 meters (650 feet) from any pipe systems. Such an exemption undoubtedly involves no danger to the underground structures. Where the railway line is so constructed that the rails are practically insulated from the earth, such, for example, as a railway line on a private right of way on which the rails are set up on wooden ties entirely out of contact with the earth, exemption from rigorous voltage regulations regarding track potentials should also be made.

(*g*) *Insulated Negative Feeders.*—If the regulations prescribe certain specific and definite voltage limitations that must be complied with, it will not be best to specify the manner in which such regulations are to be met. In order, however, to make it readily possible to further improve conditions at a later date, if such improvement should be found necessary, and to accomplish this without any appreciable extra cost to the railway companies, it would be well to require that in any future construction wherever negative feeders are installed at all they should be installed as insulated feeders in such a way that they may, when necessary, be converted into what has been defined in this paper as an insulated negative feeder system. The insulation of negative feeders in this way is practically no more

expensive than the installation of uninsulated feeders, so that no hardship would be imposed on the railway company by such requirements; on the other hand, in case future experience showed it to be necessary to still further reduce voltage drops, it would be a decided advantage to the railway company to the have feeders installed in this way.

6. RESPONSIBILITIES OF OWNERS OF UNDERGROUND UTILITIES REGARDING ELECTROLYSIS

In considering the subject of regulations for the mitigation of electrolysis, it should be borne in mind that while the railway companies are chiefly responsible for reducing stray currents to as low values as are commercially practicable, the owners of underground utilities also must be considered to have certain responsibilities, particularly in so far as new construction work is concerned in territory already occupied by electric railways.

There are a number of things that pipe and cable owning companies can do at a very slight additional expense that will go very far to reduce electrolysis trouble, provided such measures are taken at the time the pipes or cables are installed. For example, in new work or repairs, pipe lines should be laid as far as possible from railway tracks. Where the density of service connections is sufficient to justify the use of two mains, one on each side of the street, these should be laid down in order to eliminate the necessity for running services across under the railway tracks. This is quite common practice in many places where the utilities are highly developed, and it could frequently be extended in many instances with considerable improvement in local electrolysis conditions. Further, in laying new mains or repairing old ones, it is very simple and inexpensive to install a sufficient number of insulating joints largely to reduce stray currents in that portion of the pipe network, and such construction should be encouraged in every practicable way.

Wherever it is necessary to run service pipes across the street under railway tracks, care should be taken either to lay them as far as practicable below the tracks or else to provide substantial insulation between the service pipe and the track or between the service and the main by means of insulating joints; the latter will generally be found cheapest and most effective.

7. LIMITATION OF PIPE DRAINAGE

In view of the fact that excessive drainage of current from one pipe system may set up a condition of serious danger in a neighboring system, measures should be taken to so restrict the drainage of current from any one underground metallic structure that it will not be maintained at a potential sufficiently lower than surrounding structures to cause any serious injury thereto.

8. ADMINISTRATION OF REGULATIONS

Where regulations governing electrolysis mitigation are necessary, they should preferably be enacted and administered by State authority, where the necessary administrative machinery is available. In the absence of such administrative authority, however, the cities in which the utilities operate, should take the initiative. The Federal Government, while competent to carry out engineering investigations bearing on the problem as it is now doing, can not undertake to prescribe or administer regulations. Where State public utility commissions are in existence, they constitute the most logical and competent authority to deal with this subject. Such State commissioners are not only able to deal with the subject in a broader and more comprehensive way than the majority of local bodies, especially in smaller cities, but their freedom from the influences of local interests will often enable them to deal more wisely and justly with all companies involved.

It is in the highest degree desirable that regulations be made as few and as simple as possible, to the end that the various utilities concerned may enjoy the greatest freedom of action consistent with safety to the underground structures.

The present apparent necessity for regulations governing this subject is due to the lack of cooperation in the past between the railway companies and the owners of underground utilities. If the various interests concerned, and particularly the railway companies, would show a greater disposition than they have commonly done to meet the issue, and instead of practically ignoring the subject, as has been too often done, would treat the matter as one of the engineering problems connected with the operation of street railways, the need for stringent regulations would be largely eliminated with advantage to all concerned. In the ab-

sence of such a far-sighted policy, however, compulsory and perhaps more or less burdensome regulations will become inevitable.

VI. SUMMARY

Among the more important conclusions brought out in the foregoing paper are the following:

1. The electrolysis problem was for a long time neglected in America, and partly as a result of this, is now more serious than in those European countries which early met it by Government regulations. During the last few years, however, much greater attention is being given to this subject by railway companies generally.

2. Electrolysis may give rise to a number of different classes of injury, such as fires, explosions, and damage to concrete structures. However, the damage from these effects is in the aggregate relatively small. By far the greater portion of the damage due to electrolysis is that arising from corrosion of underground pipes and cables. In particular, electrolytic damage to concrete structures is to be feared only where voltage conditions are exceptionally severe, or in the case of comparatively low voltages when salt has been added to the concrete either during or after construction.

3. In general, those remedial measures that are applicable to pipe systems should be regarded as secondary means of mitigation of electrolysis trouble, the principal reliance being proper construction and maintenance of the railway return circuit. In special cases, however, mitigative measures may be applied only to the underground structures.

4. Of the mitigative measures applicable to pipes only a few of those that have been advocated have found much application. The two most commonly applied are the installation of insulating joints and the use of pipe drainage. Both these methods are valuable under certain conditions, the former particularly where new pipes are being laid and the latter for application to isolated pipe systems without insulating joints and where no other underground utilities are present to cause complications. In most cases, however, these systems should be restricted to use as auxiliary means of protection, after reasonable precautions have

been taken to reduce potential drops in the tracks to as low values as are economically practicable. In any case where pipe drainage is used, the drainage should be through the medium of insulated feeder systems, so adjusted as to take the minimum possible current from the pipes at all points.

5. Of the methods applicable to railways the most important of those which have been thoroughly tried out are the adequate maintenance of track bonding, the use of a proper number and location of power houses or substations, and, where the carrying capacity of the rails is not sufficient to return current to stations without excessive drop, the use of insulated negative feeders for the return of such current, these latter being much more economical than uninsulated feeders where large reductions of potential drop are required. The three-wire system has proved effective in relieving electrolysis and should prove satisfactory from the electrolysis standpoint where operating conditions are favorable to its use. Thus far, however, too little experience has been had with this system to justify more than tentative conclusions.

6. Such remedial measures as have been adopted in this country have usually been applied to the pipes, and in general they have proven much less effective than measures used in certain foreign countries where regulations limiting voltage drops in the negative return have long been in effect and have been accompanied by substantial freedom from electrolysis troubles. Experience both here and abroad indicates that such limitation of voltage drop is necessary to a satisfactory solution of the problem.

7. In defining the voltage limitations either the all-day average value or the average value for a period not less than one-half hour may be used; the former, however, is preferable, since it affords the best criterion of the actual danger involved and is also more satisfactory from the standpoint of the railway companies. A shorter period than half an hour is too short to give a satisfactory basis for voltage regulations that are to be applied to the railway systems.

8. In fixing voltage limitations some plan analogous to the zone system should be adopted, the voltage limits prescribed for the various zones being determined largely by the degree of development of the underground utilities in the various zones.

9. The voltage drops either in the tracks or in the pipes, and earth may be used as the basis of fixing limitation, but in general the latter is to be preferred.

10. Under most conditions over-all voltages in railway tracks should be limited to about 2 to 4 volts, and the potential gradients should in general be restricted to about 0.3 to 0.4 volt per thousand feet, these figures being all-day average values, or to corresponding values based on averages for a period of not less than half an hour. The higher over-all voltage limit will generally apply to the longer feeding distance and outlying districts, while the higher potential gradient limit can be permitted where feeding distances are relatively short. Potential drops on pipe systems should be, roughly, half of these figures.

11. In order that ready determination of voltage drops can be made at any time, potential wires should be installed running from some central point to selected points on the railway or pipe networks. These points should include the points of approximately highest and lowest potential, and preferably also some intermediate points.

12. Exemption from any regulations regarding track voltages should be made in special cases as set forth in this paper, where local conditions make it improbable that any serious damage would result.

13. Any regulations governing electrolysis mitigation should be made to apply not alone to the railway system, but should also define the responsibilities of the owners of underground utilities, since the latter can often contribute materially to the diminution of the trouble at a practically negligible cost.

WASHINGTON, March, 1918.

APPENDIXES

APPENDIX 1.—EXTRACT FROM PAPER ON "MEANS FOR PREVENTING ELECTROLYSIS OF BURIED METAL PIPES" [a]

* * * Having referred to the method of preventing electrolysis, which has been employed on a portion of the pipes in Boston and in some other American cities for several years, and to some of the erroneous ideas on the subject, we may now present the outline for another method of minimizing the danger. No description of this plan has ever before appeared in print. It is furthermore attractive as lying entirely within the power of the railway companies to adopt. It is not excessively expensive and it does not involve connections with other companies' property, nor the mutual coopera-

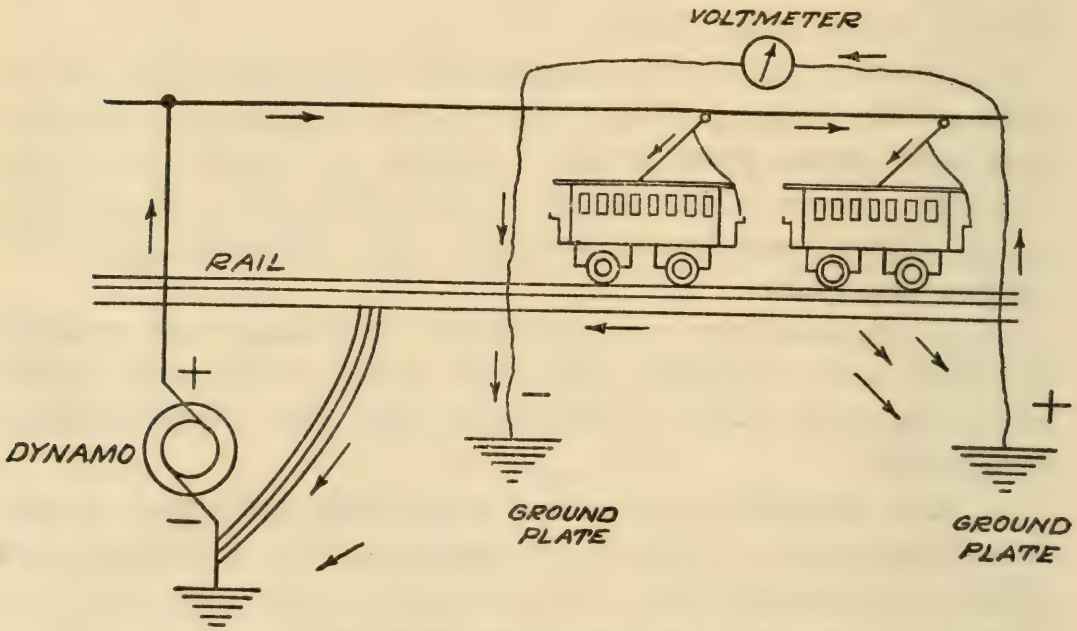


FIG. 37.—*Diagram showing the difference in potential along an electric railway*

tion of cities or corporations. By this method the tracks of the railway will also be preserved from electrolytic action.

In order to bring the principle clearly before the reader, the writer would call attention to a fact generally known, but often ignored. In all cities where electric railways operating the single-trolley system are in use, and especially where trouble from electrolysis has been discovered, it is found that the earth in one section of the city has a different electrical condition from that in certain other sections. If an insulated wire, having included in its length a suitable galvanometer or voltmeter, is extended between a ground plate located near the railway power house and another ground plate located a mile distant from the first plate, as shown in the diagram marked Fig. 1 [identified

[a] By Isaiah H. Farnham, published in Cassier's Magazine for August, 1895.

as Fig. 37 in this publication], a difference of potential will be found to exist between these plates. If the dynamo is connected with its positive pole to the trolley, the ground plate situated at the greater distance will be positive to the plate near the power house.

Some of the fire underwriters recognize this difference of potential as a danger, and they attempt to rule against it. The writer has known such difference of potential to reach 50 volts and more. The earth in the distant territory is, so to speak, saturated with positive electricity, while near the station it is being "pumped out" or made negative by the dynamo. This want of a level, or balance, in the electrical condition of the earth, leads to a flow of the current from the higher to the lower electrical level, much as would occur if water should replace the electricity. In flowing, the electricity finds its way into pipes and cables, and, on leaving them at the lower level, causes the electrolytic action.

Fig. 2 [identified as Fig. 38 in this publication], on the next page, will, by analogy, fairly illustrate this want of electrical balance or level in the earth. The line A represents the surface of the earth; B, the surface of a flood of water produced by a heavy rain, and flowing to a low plane where a pump is drawing the water from the earth in a limited district.

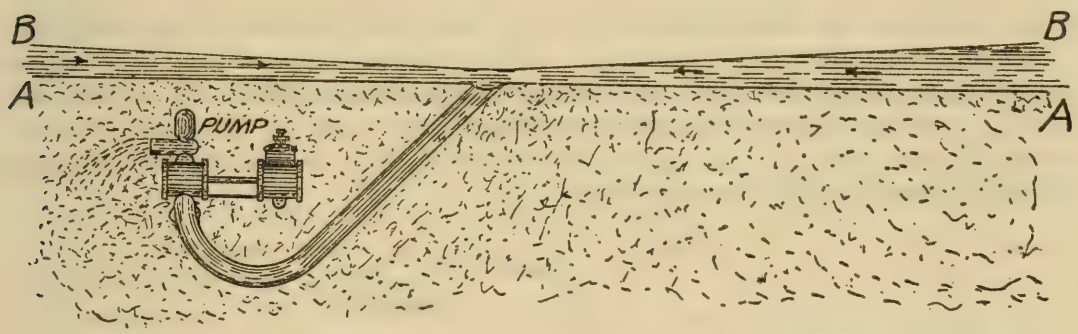


FIG. 38.—*Diagram illustrating the want of electrical balance in the earth*

If, now, we can preserve a level or balance in the electrical condition throughout the city, or, in other words, prevent a difference of potential, there will be no disposition for a current to flow from one portion of the city to another. It is the purpose in the plan now proposed to accomplish this equalization of potential as nearly as possible. To illlustrate by the water analogy, Fig. 3 [identified as Fig. 39 in this publication] shows the flood of water being pumped from many points on the surface of the earth by pipes of proper size, so that there is substantially no difference of water level, and therefore no flow from one distant point on the earth to another. A comparison of this figure with the one above it will render the point clearer.

As may be anticipated by a study of the principles already set forth, the new method consists in extending from the negative or rail side of the dynamo an insulated return wire, either on poles or underground, throughout the entire length of the railway, including all cross-town or branch tracks. This return wire is to be of such size as to properly carry the current and to maintain the return path at a comparatively low resistance. For a track extending 3 miles in any one direction from the power house a No. 0000 copper wire would give a resistance of but 1 ohm from the most distant point. Two such wires, about one-third inch in diameter each, would not seem excessive in cost, and would render the maximum resistance but one-half ohm from car to power house.

In large railway systems a still heavier main return may be employed. From this general return wire or system of wires frequent connections would be extended to the track system, say one at every other pole (200 feet). Let these connections between the general return wire and the rails be of such size, or shape, as to cause the resistance from the rail at the nearest point to the power house to be the same, no more nor less, than from the most distant rail connection to the power house; that is, with such a system, if the resistance of the circuit from the rail, 3 miles distant, to the power house

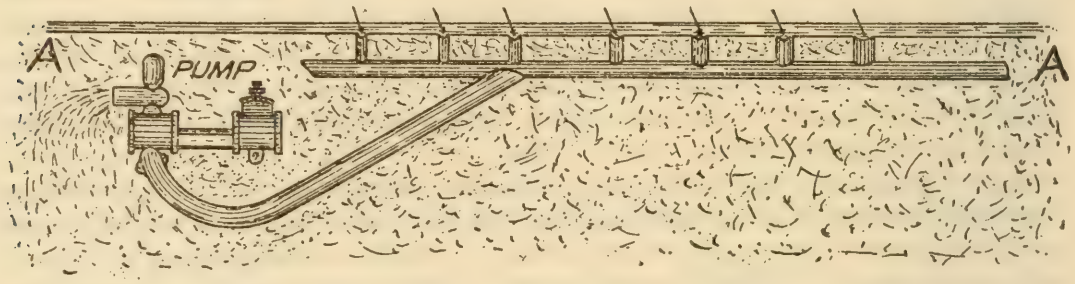


FIG. 39.—*Diagram illustrating an example of electrical balance*

is one-half ohm, the resistance from any other point along the route of the track shall also be one-half ohm to the power house. Allow no ground connection on the dynamos and no direct connection to the rails without the proper resistance. Fig. 4 [identified as Fig. 40 in this publication] roughly represents such a system. It should be understood that the rails are to be suitably bonded under this, as other systems using the rails for a portion of the electric circuit.

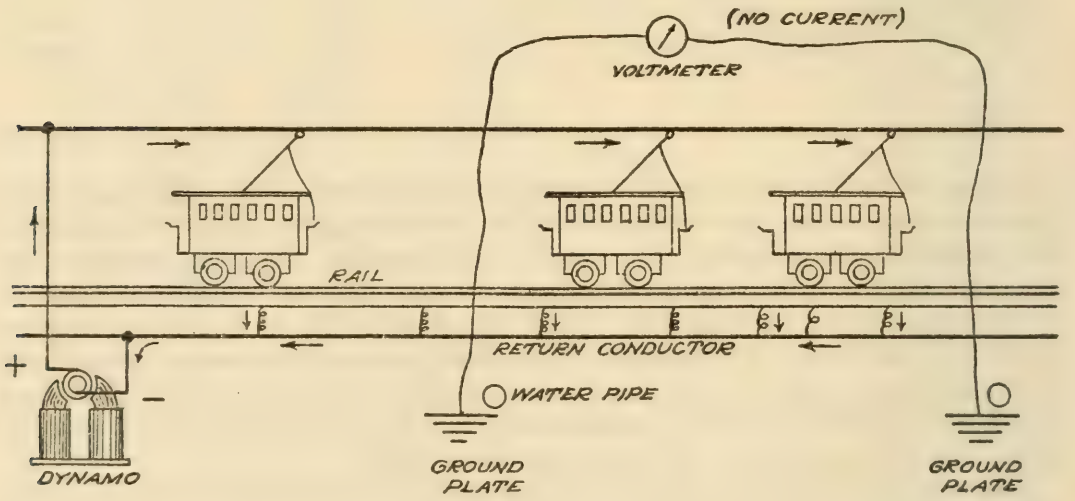


FIG. 40.—*A system with which electrolysis of buried pipes is avoided*

If, now, we imagine an approximately uniform distribution of cars, there can be no rise or fall of potential in the earth except at the very limited areas between the several points where the rails are connected to the general return wire system. Cars are not, of course, equally distributed over a city, and, therefore, perfect results can not be reached by carrying out this plan, but to adopt it is certainly working in the right direction, and as the distribution of cars approximates uniformity, the advantages of the system will approach the maximum. On the other hand, with

the present usual manner of connecting the return wires to the tracks there never can be a condition where a difference of potential will not exist between different sections of a city, no matter how nearly perfect the rail system is constructed as a return conductor, and, therefore, there can be no elimination of current passing from a higher to a lower potential throughout a city; and, of course, as the currents pass through the earth, pipes are brought into the path, and constitute a portion of the electric conductor, with all the possibilities of electrolysis wherever, from a poor joint or for other reasons, the currents leave the pipes for the damp earth on their way to the negative side of the dynamo.

This system of returning the railway current will accomplish several desirable ends: (1) It will allow but very little current to enter the earth and flow therein; (2) the current through the earth being minimized, electrolysis will to that extent be prevented; (3) having by this means reduced the danger of electrolysis to small proportions, it will be comparatively easy to take care of the remaining danger, if such be found, by resorting to the means described in the previous paper; (4) in addition to practically overcoming the danger of electrolysis, the annoyance to telegraph, telephone, burglar alarm, and other grounded circuits, due to difference of potential in different sections of a city, will be incidentally removed.

The equi-potential return system just described has so far been tried in a New England city as to indicate practically that the benefits claimed for it may be confidently expected.

APPENDIX 2.—PUBLICATIONS OF THE BUREAU OF STANDARDS RELATING TO ELECTROLYSIS

Technologic Paper No. 15: Surface Insulation of Pipes as a Means of Preventing Electrolysis; by Burton McCollum and O. S. Peters.

Technologic Paper No. 18: Electrolysis in Concrete; by Dr. E. B. Rosa, Burton McCollum, and O. S. Peters.

Technologic Paper No. 25: Electrolytic Corrosion of Iron in Soils; by Burton McCollum and K. H. Logan.

Technologic Paper No. 26: Earth Resistance and its Relation to Electrolysis; by Burton McCollum and K. H. Logan.

Technologic Paper No. 27: Special Studies in Electrolysis Mitigation, No. 1; by Dr. E. B. Rosa and Burton McCollum.

Technologic Paper No. 28: Methods of Making Electrolysis Surveys; by Burton McCollum and G. H. Ahlborn.

Technologic Paper No. 32: Special Studies in Electrolysis Mitigation, No. 2; by Dr. E. B. Rosa, Burton McCollum, and K. H. Logan.

Technologic Paper No. 52: Electrolysis and Its Mitigation; by Dr. E. B. Rosa and Burton McCollum.

Technologic Paper No. 62: Modern Practice in the Construction and Maintenance of Rail Joints and Bonds in Electric Railways; by E. R. Shepard.

Technologic Paper No. 63: Leakage of Currents from Electric Railways; by Burton McCollum and K. H. Logan.

Technologic Paper No. 72: Influence of Frequency of Alternating or Infrequently Reversed Currents on Electrytic Corrosion; by Burton McCollum and G. H. Ahlborn.

Technologic Paper No. 75: Data on Electric Railway Track Leakage; by G. H. Ahlborn.

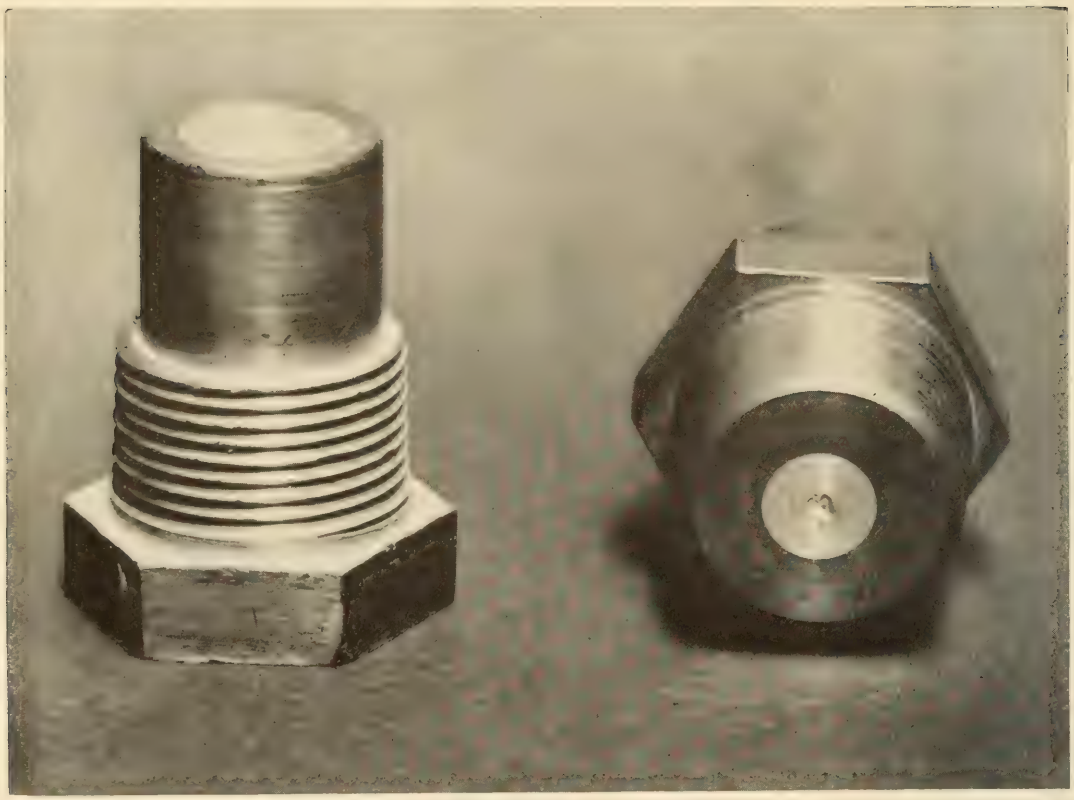


FIG. 1.—*Fusible tin boiler plug*

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 53

AN INVESTIGATION OF FUSIBLE TIN BOILER PLUGS

BY

GEORGE K. BURGESS, Physicist

and

PAUL D. MERICA, Assistant Physicist

Bureau of Standards

ISSUED OCTOBER 15, 1915

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AN INVESTIGATION OF FUSIBLE TIN BOILER PLUGS

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I. INTRODUCTION

The fusible boiler plug in its usual form consists of a brass or bronze casing with external pipe thread, filled from end to end with a fusible metal or metal composition, which has a melting point around 200° C (390° F); two such plugs are shown in Fig. 1. These are fitted at various places into the boiler, either in the flues, tubes, or combustion chamber, in such a position, however, that they are about 1 inch or more above the dangerous low-water level, with one end on the fire and one end on the water side. As long as the water level in the boiler is above these plugs the temperature of the latter remains below the melting point of the filling (at 150 pounds boiler pressure the temperature is about 180° C or 357° F), but if the water falls much below the level of the plug, opportunity is given for a local overheating in the

vicinity of the plug. The filling of the plug then melts and is blown out.

The fusible plug seems to be an old English invention and to have been in use for many years. It has, in fact, been required to be installed in all steam vessels of the American merchant marine since 1852, and is now required in all boilers except pipe, flash, or coil boilers on vessels subject to inspection by the Steamboat Inspection Service, Department of Commerce. This inspection includes approximately 11 850 boilers requiring installation of boiler plugs.

Fusible plugs are also used elsewhere than in boilers of the American merchant marine. They are used in many but not all factory and locomotive boilers in this country and abroad, but are not generally used in marine boilers abroad.

They are also not used in the United States naval service, the practice there not favoring the installation of safety devices of any sort, fusible plugs or otherwise, as it is considered that there presence fosters negligence. This opinion—at least in so far as it concerns boiler plugs—appears to be shared also by many railroad authorities.

1. SPECIFICATIONS FOR FUSIBLE TIN BOILER PLUGS

Four typical sets of specifications for fusible tin boiler plugs are given in Appendixes 2 and 3. In Appendix 2 are given the existing specifications of the Steamboat Inspection Service, of the Interstate Commerce Commission, and the recommended specifications of the American Society of Mechanical Engineers. In Appendix 3 are given the specifications of the Steamboat-Inspection Service in force in July, 1914, at the time the present investigation was begun.

Tin seems to be the metal used at present almost exclusively as the fusible constituent of such plugs, and is required by the above specifications. It would seem to be in this respect a desirable metal, having a low melting point, being only slightly corrodible and easily obtained pure. Its desirability in this respect is nevertheless to some extent called in question by the results of the investigational survey of fusible tin boiler plugs, which was

made at this Bureau, from June, 1914, to March, 1915. These specifications will be referred to again briefly in Section II, and also in Section IV after describing the experiments at this Bureau.

II. EXAMINATION AND INVESTIGATION OF PLUGS

On May 11, 1914, a boiler of the steamship *Jefferson* exploded, causing the loss of life of several persons. Investigation showed this explosion to have been due to low water and consequent overheating of the boiler plates. This should have been indicated by the melting of the filling of the Banka tin plug in that region, which plug, however, was found to be unmelted and apparently or at least superficially sound.

At the suggestion of the Secretary of Commerce, this plug was sent to this Bureau for determination of its cause of failure. It was sawed open longitudinally and was found to contain traces only of the original tin, embedded in a dirty, greenish-white matrix. A photograph of this central longitudinal section is shown in Fig. 2, in which the light regions represent the remaining tin. The matrix was found to be largely tin oxide, SnO_2, which upon test showed a melting point above 1600° C (about 2900° F). This oxide was distributed in such a form and quantity that it held the pressure of the boiler, and would not have melted until the bronze of the casing and even the steel of the boiler had melted. When reliance is placed upon such a plug to give warning of dangerous boiler conditions it is to be looked upon as an actual source of danger instead of safety.

The question arose then, To what is the presence of tin oxide to be ascribed; was it there originally; has it been formed by corrosion; and, if so, is the cause for its comparatively rare occurrence in such plugs to be sought wholly in the different operating conditions of the boilers, or is a fault in the method of manufacture of these plugs at least partially responsible? A search in the literature failed to reveal any reference to failures of fusible tin plugs of this sort, except vague statements that they were not entirely reliable, due to the formation of boiler scale on the inside and soot on the outside, and a statement that the filling was likely to change its melting point during service. No data could be found concerning the oxidation of tin at higher temperatures.

A request was then made to the Steamboat-Inspection Service that more plugs be sent to the Bureau for test, both new plugs and also those which had been removed by the inspectors, in order that by an inspection of these plugs information might be obtained bearing on the points raised above. In answer to the request 1050 plugs were received, of which about 100 had been in service varying from 4 to 12 months, and representing the products of 105 firms.

These plugs were first examined to ascertain whether their dimensions corresponded to the specifications of the Steamboat-Inspection Service. They were then sawed open axially through the center and the form and condition of the filling observed, particular attention being paid to the presence of oxide, scoriae, blowholes, and other faults originating either in the manufacture of the plugs or during their service.

1. DESIGN AND CONSTRUCTION

The specifications require certain minimum values of the diameter of the tin filling at both ends. In three plugs from three firms these dimensions were less by one sixty-fourth inch than the prescribed value.

The specifications in force at the time these plugs were manufactured called for a bore "tapering evenly from end to end of filling." (See Appendix 3.) Of 1033 plugs examined in this respect, 97 did not correspond to this specification. These were manufactured by 30 firms. Of these, 27 contained fillings having ribs projecting into the casing, 3 contained threaded fillings, and 22 contained fillings which were not tapered along their entire length. In four plugs from the same manufacturer the bore of the casing had not been machined after casting and the filling could be easily dislodged from the casing.

It may be noted here that the correct design of such a plug is of more importance than might be casually supposed. It is shown below that, owing to the difference in the coefficients of expansion of the casing and of the filling of such a plug and to the existence of an allotropic change in tin at about 160° C (320° F), there will be interplay between casing and filling unless

the design is such as to support the filling rigidly in the casing and unless the adhesion between the two is excellent.

A smooth bore "tapering evenly from end to end" is from this consideration not to be recommended, and, indeed, the Steamboat-Inspection Service has recently allowed a fine inside thread. It is hardly evident, however, why a thread should be allowed, and not other types of recess or projecting shoulder, to keep the tin filling rigidly in place.

The new plugs, about 950 in number, were all of sound appearance, and none showed the presence of oxide or scoriae in the tin filling. A number of the plugs contained minute blowholes, and about 10 of the 950 plugs showed blowholes of from $\frac{1}{8}$ to $\frac{3}{16}$ inch in diameter. The inner surface of these blowholes was always clean and bright.

2. TYPES OF DETERIORATION

The condition of the tin in the plugs which had been in service varied greatly. A few of the fillings were piped or showed blowholes, the surfaces of which were clean and bright.

1. There were 22 plugs from 10 firms which showed sound fillings that had remained apparently absolutely unchanged after a service of 12 months in most cases.

2. In 47 plugs from 21 firms the filling had been partially melted away at the fire end, as shown in Figs. 3 and 4. The fillings were otherwise sound. In about 10 of these plugs a scale of oxide coating had been left on the inside of the casing bore as can be seen in Fig. 4. In the other cases the fire end of the casing bore was clean.

3. In 11 plugs from 6 firms (besides those of class 5 (a) below) the filling had expanded and protruded at the fire end (small end) or at both ends. This is shown in Figs. 5, 6, and 12. The fillings were sound except that in 9 cases a layer of oxide was to be found between the casing and filling, as is shown in Fig. 7. This layer is usually seen to start from the fire end. The oxidation at the edge of the filling was probably preceded by a loosening of the plug in its casing which allowed access of flue gases. This is discussed below.

4. Seven plugs were either corroded or pressed in at the water end, the appearance of one of which is shown in Fig. 8. Although the inside surfaces of the tin were sometimes corroded, it is probable that this peculiar form had been assumed under the pressure of the boiler while the tin was at a temperature at which it was semiplastic, i. e., between 195° and 230° C. In one case the tool marks could still be seen on the inside (water side) surface, which was sunk about 5 mm. at the center.

5. In 14 plugs, from 8 firms, nonmetallic inclosures or incrustations were found in the filling. Since this mass was found to be in most cases, where not otherwise noted, practically pure tin oxide, SnO_2, contaminated at times with traces of ZnO and CuO, it will hereafter be referred to as it was under (2) and (3) as "oxide." This oxide occurred in several forms.

(*a*) In 4 plugs from one firm the oxide was practically pure SnO_2 with traces of zinc and lead and no traces of sulphates, chlorides, or nitrates, and occurred in the form of a network, proceeding from the water end toward the fire end. This type is shown in Figs. 9, 10, 11, 12, and 13, which show successive stages of the progress of the oxidation. Of these Fig. 9 is of plug No. 56, Figs. 10 and 11 of plug No. 872, and Figs. 12 and 13 of plug No. 40. The original plug from a boiler of the steamship *Jefferson* shows a very much more advanced state of this type of oxidation. (See Fig. 2.)

It is obvious from the following considerations that this oxidation occurred in service and that the oxide was not poured in with the tin originally:

(1) The plug is always expanded outward at oxidized end.

(2) The oxidation always starts from the water end of plug and becomes less marked toward the fire end.

(3) This oxide is immediately visible upon exposing a surface of the "tin," and a plug containing it in this form could not escape rejection when the plug ends were machine finished.

(4) It has been attempted and not found possible to pour tin plugs in which oxide veins or granules of such coarse texture are visible. In such attempts to do this the tin was first badly oxidized and then poured at temperatures varying from about 300° to 500° C (600° to 900° F).

(*b*) In 10 plugs from 7 firms the fire end of the plug was filled for a third to one-half of the distance from the end with a solid adherent mass of what was in many cases impure oxide of tin with traces of sulphates, zinc, lead, and copper. The characteristic appearances of these plugs are shown in Figs. 14, 15, 16, 17, and 18.

6. Two plugs had the appearance shown in Fig. 19. These plugs had evidently been arrested by the inrush of "cold" water in the very act of blowing out while at a temperature in which they were semiplastic.

The classification here described is summarized in Table 1.

TABLE 1

Types of Deterioration

Condition of plug or type of deterioration	Plugs belonging to category of column 1	Manufacturers whose products belonged to class of column 1
1. Filling sound	22	10
2. Filling sound, but partially melted away	47	21
3. Filling expanded	11	6
4. Filling corroded or pressed in at water end	7	3
5, *a*. Filling had undergone "network oxidation"	4	1
5, *b*. Filling partially gone and casing filled partly with nonmetallic matter, oxide of tin, plaster of Paris, etc	10	7
6. Fillings arrested in blowing out	2	2

It was evident that of the approximately 100 used plugs examined only 7 contained the incrustation or oxides in sufficient quantity and in a form which would have prevented the blowing out of the plug at the melting point of tin. These were plugs 40, shown in Figs. 12 and 13; 43, similar to 40; 9, shown in Fig 14; 27, shown in Fig. 16; 122, shown in Fig. 15; 1045, shown in Fig. 17; and 1047, similar to No. 1045.

In all of these cases the incrustation or the network of oxide would probably have held the boiler pressure even after the melting of the tin which still remained in the plug. These plugs were dangerous plugs.

3. PURITY OF TIN AND RELATION TO DETERIORATION

In order to relate, if possible, the types of failures just enumerated to the purity of the tin in the fillings, the melting point of a number of the used plugs as well as of the new ones was taken. It is well known that the presence of metallic impurities changes the melting point of a pure metal, and, indeed, the melting point may be used, as it was in this case, as a criterion of the purity of a metal. Impurities in small amounts, such as lead, zinc, bismuth, cadmium, and copper, lower the melting point of tin, whereas iron and antimony raise it. (See Bornemann, Die binären Metal legierungen, 1909–1912.)

As very little material was available from a plug, these determinations had to be made with small quantities; therefore several were made with a modified form of the micropyrometer, described in this Bureau's Scientific Papers Nos. 198 and 205, by Burgess and by Burgess and Waltenberg, respectively,[1] in which method only a minute amount of material is required. As the optical pyrometer could not be used at this temperature, these determinations were made by calibration of platinum strip temperatures in terms of heating current. This was done for temperatures of 231°.9 C (melting point of tin), 271° C (bismuth), and 320°.9 C (cadmium). For each determination minute pieces of "Kahlbaum" tin (highest grade of purity) and of the tin for test were placed side by side on the platinum strip and observed by perpendicularly reflected light through a microscope.

The current through the platinum strip was gradually increased, and by noting the values of the current at which the pure and the test tin melted, respectively, the difference between their melting points could be computed from the calibration curve of platinum strip temperature and heating current. This method was satis factory only for small differences of temperature of one or two degrees and was in no case as accurate as the other determinations described below.

The majority of the thermal purity tests, however, were made as freezing point determinations by a direct cooling curve method

[1] Bulletin Bureau of Standards, 9, p. 475, 1913; and 10, p. 1, 1913.

requiring only 2 or 3 grams of the material. A small glass tube of about 6 mm diameter was fused shut at one end and 2 or 3 grams of the tin sample to be tested was inserted and melted at the bottom of the tube. A copper-constantan thermocouple, made of wires of 0.3 mm diameter inclosed in a much smaller, thin-walled glass tube, was then placed in the molten tin, and the larger tube with tin and thermocouple immersed in an oil bath, 15 cm deep, which was heated with a Bunsen flame. The ends of the couple were attached through ice-cold junctions to either a potentiometer or a milli-voltmeter of high resistance, 400 ohms, by which the emf of the thermocouple could be measured. The temperature of the bath was then allowed to fall, by removing the Bunsen flame, and readings of the emf were taken every 15 seconds on the potentiometer. The curves of time and emf so taken showed well-defined arrests in all cases except for those with a large percentage of impurity (for example, there was 8 per cent lead in one case) when the solidification took place over a wide temperature interval. The values obtained in taking one of the cooling curves of pure "Kahlbaum" tin are given below.

Freezing of Pure Tin

[Potentiometer (emf) readings taken every 15 seconds]

Millivolts	Differences	Millivolts	Differences	Millivolts	Differences
10.19	0.03	9.99	0.01	9.97	0.01
10.16	.04	9.98	.00	9.96	.03
10.12	.03	9.98	.00	9.93	.02
10.09	.04	9.98	.00	9.91	.02
10.05	.04	9.98	.00	9.89	.06
10.01	.02	9.98	.01	9.83	....

The "freezing" point of this sample was at the "arrest" at 9.98 millivolts. The thermocouple was calibrated under the same conditions at the steam point (about 100° C) and at the melting point of pure Kahlbaum tin taken at 231.9° C. The values on fairly pure tin could be repeated generally to within ±0.01 millivolt or within ±0.15° C, and in fact the arrests on successive cooling curves of Kahlbaum tin repeated more closely.

Chemical analyses were then made on some of the samples to check the results of the thermal data.

In Table 2 are given various characteristics of the fusible plugs examined, including time of service, freezing point, chemical analysis, and reference to photographs. The manufacturers are represented by letters in column 3.

TABLE 2

Characteristics of Fusible Plugs

Plug	Months in service	Steamship	Manufacturer	Freezing point of tin filling °C [a]	Chemical analysis [b]			Photograph
					Zinc	Lead	Other metals	
		USED PLUGS						
		Class 1.—Plugs Apparently Sound After Service			Per cent	Per cent	Per cent	
80	12	Verne Swain	A	232.2				
88	12	Sunshine	B	231.4				
89	12	.....do	B	228.2	0.2	1.3		
109	12	Waterford	C	228.6	.6	.5		
870	3	Panama	C	[c] 229	Trace	Trace	0	
871	4	Tug 20, N. Y. C	C	[c] 228.5	Trace	Trace	0	
873	4	.....do	C	[c] 229	Trace	Trace	Trace Cu	
1035		Seaboard	C	227.4	1.8	Trace		
1036		.....do	C	226.8	1.3	.1		
1037		.....do	C	226.8	.9	.2		
1039	4	West Farms	C	229.8	.7	Trace		
1048		Tug S. Q. Brown	P	229.0	.3	.7		
1049		.....do	P	228.4	.3	1.2		
1050		.....do	P	228.3	.4	.8		
		Class 2.—Plugs of which the Filling was Partially Melted Out at the Fire End						
102				230.2				
2	8	Andasti	D	230.8				
3	6	Geo. B. Leonard	E	229.8				
5	5	Sir T. Shaughnessy	F	230.3				
6	7	Jas. T. Martin	D	228.4	.8	.1		
7	7	Joe D. Morrow	G	230.1				
10	8	Kniskle Bros	D	230.6				
19	12	Game Cock	H	229.4	.6	.4		8

[a] Pure Kahlbaum tin, Banka tin, and Straits tin have a freezing point at 231.9° C.

[b] Blanks signify that no analysis was made for the metal or metals in that column. The group "Other metals" includes silver, mercury, copper, bismuth, antimony, arsenic, iron, aluminum, chromium, nickel, manganese, and magnesium.

[c] These determinations are accurate only within ±1.0°.

TABLE 2—Continued

Plug	Months in service	Steamship	Manufacturer	Freezing point of tin filling °C	Chemical analysis			Photograph
					Zinc	Lead	Other metals	
		USED PLUGS—Contd						
		Class 2—Continued			Per cent	Per cent	Per cent	
20	5	F. B. Jones	H	228.6	.7	.2	.....	.....
23	12	Dallas City	H	229.8	.....	.....	.....	.....
50	.....	Chesapeake	I	231.4	.....	.....	.....	.....
94	5	Columbia	J	230.4	.....	.....	.....	4
99	12	Huron	K	230.4	.....	.....	.....	.....
1030	3	Jamestown	L	232.0	.....	.....	.....	.....
1031	3	.....do	L	231.9	.....	.....	.....	.....
1032	3	.....do	D	230.0	.....	.....	.....	.....
1044	3	Alaskan	R	229.6	.5	.7	.....	.....
1046	3	.....do	R	230.0	.6	.8	.....	.....
		Class 3						
81	12	Verne Swain	A	230.1	.....	.....	.....	.....
57	12	City of Atlanta	C	230.3	.....	.....	.....	.....
69	12	Red Spot	M	231.1	.....	.....	.....	.....
71	12	Spottsville	M	231.9	.....	.....	.....	.....
82	12	C. H. Organ	A	231.0	.....	.....	.....	.....
68	12	S. P. Gillett	N	231.9	.....	.....	.....	7
84	12	C. H. Organ	A	230.3	.....	.....	.....	.....
83	12	.....do	A	229.0	.....	.....	.....	.....
85	12	.....do	A	231.9	.....	.....	.....	.....
48	.....	.....	O	230.3	.....	.....	.....	5
72	12	Commerce	P	228.7	.10	1.00	.....	6
		Class 4.—Plugs Corroded or Pressed in at Water End						
19	12	Game Cock	H	229.4	.6	.4	.....	8
20	5	F. B. Jones	H	228.6	.7	.2	.....	.....
		Class 5.—Plugs Containing Oxide						
		Subclass (a), Network oxide						
40	12	Gowanus	C	230	.5	Trace	0	12, 13
43	12	.....do	C	225	3.5	0	0	.....
56	12	City of Augusta	C	229.9	.4	.....	.....	9
872	3	Tug 20, N. Y. C	C	225	4.2	0	0	10, 11

TABLE 2—Continued

Plug	Months in service	Steamship	Manufacturer	Freezing point of tin filling °C	Chemical analysis			Photograph
					Zinc	Lead	Other metals	
		USED PLUGS—Contd						
		Class 5—Continued						
		Subclass (b), Containing solid "oxide" or other nonmetallic inclusion						
					Per cent	Per cent	Per cent	
9	8	Kniskle Bros.	D	230.0				14
27	3	Shaver	H	228.6	.8	.3	0	16
122	12	J. A. Carney	H	231.9	0	0	0	15
1045	3	Alaskan	R	230.2	.6	.2		17
1047	3	.....do	R	228.0	1.0	.6		
20	5	F. B. Jones	H	228.6	.7	.2		
59	12	Clevedon	P	224.6				18
73	12	Onward	N	228.2				
18	12	Bailey Gatzert	T	228.8				
		NEW PLUGS						
1034				230.8				
1038				228.3	.9	Trace		
1051				230.2				
637				c 230				
529				230.6	0	Trace	Trace Cu	
505				c 231				
479				c 230				
476				c 229				
444				c 230				
427				c 231				
421				231	0	Trace	Trace Cu	
285				c 229				
272				c 221				
202				c 232				
190				c 229				
185				220		8.3		22
178				c 230				
145				c 229				
186				225		3.1		
187				228		1.9		

A consideration of the above table shows the following facts:

(*a*) Banka tin, as required in the specifications above, was not and is not being used in the filling of a considerable number of the plugs. Analyses of four samples of Banka tin by W. A.

Cowan [2] showed the tin content to be 99.93, 99.97, 99.96, and 99.96 per cent, respectively, by difference. (See Appendix 1.)

Of about 70 melting-point determinations made on used and new plugs only 11 gave values within 0°.5 C of the melting point of pure Kahlbaum, Banka, or Straits tin.

Of 35 plugs analyzed chemically only 6 fillings showed 0.20 per cent or less impurities, or, in other words, only 6 of 35 [3] plug fillings examined chemically were composed of *any* variety of high-grade tin. (See paragraph below.)

(*b*) The principal impurities are lead and zinc. It may be noted that it is not possible that the zinc or lead, in amounts greater than the solubility of these metals, respectively, in tin at high temperatures (180° to 190° C), could have come from the bronze casing by diffusion in the solid state. By solubility is meant here the amounts of these metals which actually dissolve in the tin to form a homogeneous solid solution.

(*c*) The table shows that classes 1, 2, 3, and 5 (*b*) (p. 7) contain plugs having impure tin as well as those containing pure tin (i. e., of melting point of 231°.9). Impure tin is then *not always* a cause of oxidation or deterioration in these plugs.

(*d*) All of the four plugs, as well as the plug from the boiler of the steamship *Jefferson* mentioned on page 5, showing the network type of oxide, came from the same manufacturer, were used on four different vessels, had low melting points, and contained zinc.

4. THEORY OF "NETWORK" TYPE OF OXIDATION

An explanation of this type of failure may be found in the effect of the zinc upon the process of oxidation of the zinc-tin alloy and a consideration of the constitution of the Sn–Zn alloys will throw some light upon this peculiar phenomenon.

The equilibrium diagram, according to Guertler, is shown in Fig. 20, from which it can be seen that the solubility of zinc in tin is very small in the solid state, less probably than 0.2 per cent.

[2] Journal of the American Institute of Metals, 1914.

[3] It may be noted that since the samples taken for analysis were chosen mainly from those having a low melting point, the ratio of 6 to 35 does not express the true ratio of plugs composed of impure tin to the total number examined (1050).

By this is meant that, although alloys of tin and zinc can be made in all proportions, the zinc is not in the solid state dissolved in the tin forming a solid solution of homogeneous macro- and micro-

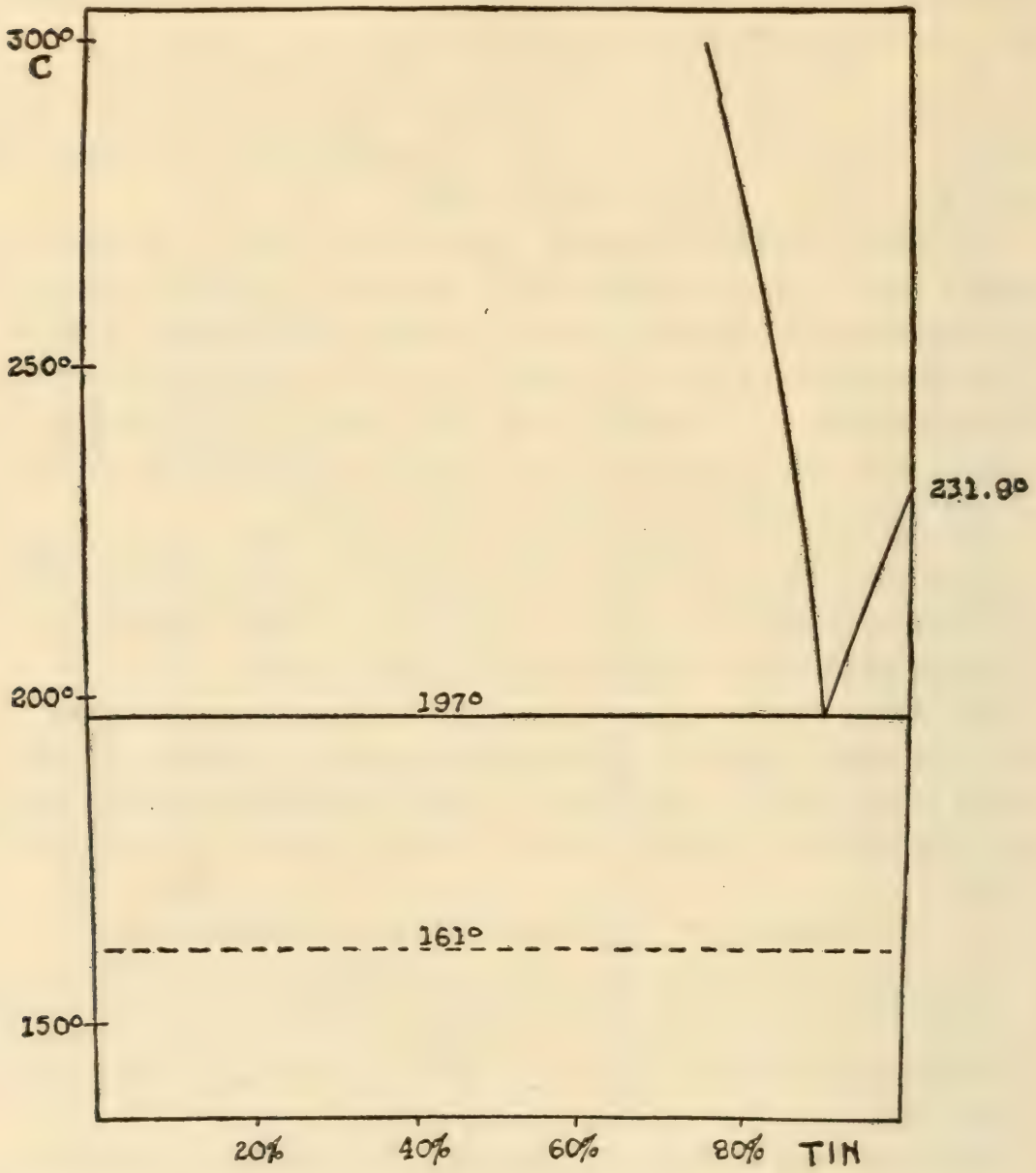

FIG. 20.—*Part of equilibrium diagram of tin-zinc*

structure. A slowly cooled alloy—tin 99 per cent and zinc 1 per cent—has the eutectic structure shown in Fig. 21, taken from a paper by Lorenz and Plumbridge,[4] in which the eutectic

[4] Z. Anorg. Chem., 83, p. 283; 1913.

crystallites of zinc (dark) can be seen distributed in the tin matrix. Upon long heating just under the eutectic horizontal at about 197° C the tin and zinc crystals coalesce, the eutectic disappears, and the structure attained is that shown in Fig, 23. This will be shown in experiments described below. In this alloy the tin crystals are surrounded by an envelope of zinc.

If, now, this alloy be brought in contact with a corrosive aqueous solution, the latter will attack the zinc first, eating its way into the plug through the grain or crystal interstices, and the tin filling finally becomes honeycombed in structure. The corrosion of the tin itself may now start from these intercrystalline canals, and the oxidation products remain, forming gradually the oxide network structure already referred to.

There is much analogy of the oxidation of this kind to that produced in Muntz metal sheathing upon exposure on a ship's bottom to salt water. Muntz metal (60 per cent copper and 40 per cent zinc) has a heterogeneous structure, and consists of two structural constituents or phases, the alpha and the beta solid solutions, respectively, the latter containing more zinc than the former. Upon exposure to salt water, material of this sort afterwards becomes so brittle that it can be crumbled up by hand. Examination shows that the salt water has attacked the beta constituent and has removed much of it, eating its way thus into the interior of the metallic mass, such that the metal consists of the original structural "framework" of alpha, throughout which the beta filling has been at least partially removed.

Naturally, if the water, in this case the boiler water, attacks neither the tin nor perhaps even the zinc, a plug which contains zinc may remain sound after months of service. It may be mentioned here that alkaline waters, such as would be produced by overaddition of soda boiler-water softener, attack zinc even at ordinary temperatures and probably corrode both zinc and tin at higher temperatures. Furthermore, the temperature of the water and plug will determine to a great extent the velocity of the progress made by the oxidation. At a higher temperature the corrosive action will be in general greater, the velocity of the

coalescence of the zinc eutectic will be greater, and what is more important, if the temperature rise above 197° C (about 205 pounds per square inch pressure), melting will take place at the boundary of the zinc and tin, the pressure inside will force the melted portions toward the fire end of the plug, thus leaving channels open for the entrance of the water from the water side. That the fillings of plugs do so travel in their casings from the water to fire end is shown in the case of plugs under class 3.

It is thus easily seen why it is that although no plugs have been found showing the network type of oxidation, which do not contain zinc, several have been found (see above table) which do contain zinc and which have nevertheless remained sound in service during from 3 to 12 months.

In the latter cases, the tin surface on the water side was found to be clean, proving that the boiler water used did not attack it, whereas in other plugs, and particularly in those in which network oxidation had taken place, the water-side surface of the tin was badly corroded. The normal pressure used in the boilers may also have been less in these cases. There is, however, also some significance in the fact that all five of the plugs showing this type of failure came from the same manufacturer. The explanation of this fact is to be sought in the simultaneous presence of zinc and absence of lead in the fillings of these plugs. This manufacturer happened to be using impure tin which, unlike most of the impure tin used by other manufacturers, contained no lead. The action of the lead in this respect is discussed below.

The formation of incrustation in plugs under 5 (*b*) is more puzzling. That this incrustation is not always entirely formed by natural means is shown, however, by the fact that analysis of it showed it to be about 96 per cent $CaSO_4$. $\frac{1}{2}$ H_2O in plug No. 122, and $CaSO_4$ was also found in plugs Nos. 1047, 1045, and 9. Since this is at the fire end, with no communication with the boiler water, the inference is that when the plug began to leak plaster of Paris was put in at the fire end to stop the leak. However, in other cases the incrustation is free from calcium and is tin oxide with traces of copper, zinc, and tin oxides containing always sulphates—usually as copper sulphate—and was probably formed by natural processes.

It is to be noticed that the tin in plugs which have oxidized in this manner is either from its melting point or analysis seen to be impure. The presence of sulphate shows that flue gases with sulphur dioxide and oxygen content have been instrumental in oxidizing the tin filling.

The explanation why some plugs containing tin fillings (see Table 2) merely melt out at the fire end leaving no oxide, and why in others the tin oxidizes and remains as oxide, is to be sought probably in the variation in operating conditions of the boilers, in variations in the kind of coal used, as, for example, in the sulphur content of the coal; also, very possibly in the devices used by the engineers in charge of boilers to stop up leaky plugs. It is possible that if plugs could be made which would not leak, this kind of deterioration would be largely eliminated.

5. TESTING OF THEORY BY SERVICE TESTS AT BUREAU

It was thought advisable to subject a number of the new plugs as well as plugs made up at the Bureau, containing definite amounts of impurities, to the action of water at high temperatures to determine what would be their behavior under these known conditions. For this purpose the plugs were put in a copper autoclave and heated for various periods at a temperature of from 180° to 195° C (350° to 380° F), in either tap or distilled water. In two cases the temperature went too high and some of the plugs of lower melting point fused. Half of each plug was heated and half saved for comparison in each case.

Of 40 new plugs heated for 195 hours, and 20 new plugs, for 140 hours in tap water, only 3 showed any change whatever—Nos. 185, 186, and 187, all from manufacturer S. These will be seen from the table above to contain lead in varying amounts. After this treatment all were somewhat distorted and covered with spongy "eruptions," illustrated in Fig. 22 of No. 185. Whereas no lead could be detected in the microstructure before heating, owing to the fineness of its distribution, after this heating the lead had coalesced as an enveloping boundary to the tin crystals. (See Fig. 23.) The plug filling was apparently only superficially oxidized.

Plugs were then made up at the Bureau of pure Banka tin, Straits tin, and Straits tin containing the following amounts of zinc and lead:

Zinc	Lead
Per cent	Per cent
0.5	....
2.0	....
5.0	....
10.0	....
....	0.5
....	5.0
0.5	1.0
2.0	1.0
5.0	1.0
0.5	5.0

These metals were melted in a fire-clay crucible in a gas furnace and poured into casings made of 1-inch brass tubing threaded on the inside. They were cast in pairs. Of each composition the first plug was poured with care taken to avoid oxidation, and the consequent contamination of the tin of the plug with oxide. After this was poured, air was forced through the melt for from three to five minutes, thoroughly oxidizing it, after which it was then poured into the second casing, effort being made in this case to introduce oxide into the filling of the plug. It was desired to determine whether the presence of oxide from the pouring aided the process of oxidation in service. It is interesting to notice that even in one of the plugs in which the oxide must have been present to the extent of about 25 per cent, it could be detected only microscopically in the structure of a polished section. No coarse macroscopic oxide structures could be produced resembling those produced in service and described above.

Some of these were then heated in tap and some in distilled water for about 500 hours at from 180° to 195° C (350° to 380° F). There seemed to be no difference in the action of distilled and the tap water on the plugs.

After heating, the plugs containing zinc or lead in amounts equal to or above 0.5 per cent were usually found cracked. Indeed, in the case of the plug filling with 10 per cent zinc, an almost perfect

inverted pyramid had cracked off and had been forced up several millimeters. This half plug is shown in Fig. 24. This is doubtless due to the stresses caused by the expansion between the tin crystals of tin-zinc eutectoid during its melting which begins at about 197° C (385° F). In some cases, particularly when lead was present, the filling had become porous, due to the melting out of the low melting eutectoid which in this case melts around 170° C (330° F).

No change could be detected in the samples of Banka and Straits tin caused by this treatment other than a slght surface oxidation.

Every plug which contained zinc and no lead showed a network structure after 500 hours in the autoclave. This is shown in Fig. 25, of a plug containing 0.5 per cent zinc. This network structure was the more pronounced the higher the zinc content and was in many cases better developed near the surface than inside. Fig. 25 shows the structure of this plug after grinding off about 0.5 mm. This plug was sawed in two and an inside surface polished. The structure of this surface, which was about 5 to 10 mm. from the water during the heating period, is shown in Fig. 26.

It appears, then, that even with ordinary tap water some oxidation of this type takes place, for if none had taken place the network structure developed by the coalescence of the zinc should have had approximately the same density throughout, which is clearly not the case, as shown in this plug.

The structure of those plugs which contained zinc and lead, after heating with distilled water, showed a much less developed network structure than those containing the same amount of zinc and no lead under the same conditions.

It was shown here and during the examination of plugs whch had been in service for periods of from 4 to 12 months, and had remained sound, that tin may contain zinc, and be heated to temperatures around 180° C or 350° F (corresponding to an average boiler pressure of 150 pounds per square inch) and still not develop the coarse coalesced "network" structure described above. This may have been partly due to the fact that the temperatures to which they were exposed were lower than those to which the plugs

of class 5 (*a*), together with those heated at the Bureau, had been exposed; but there is little doubt but that lead partially, at least, prevents the formation of this coarse "network" structure in tin containing zinc. This is shown by the fact that—

1. Four plugs (class 5, *a*) contained zinc and no lead, and had developed this structure.

2. Tin samples with zinc and no lead developed upon heating a much more pronounced network structure than those containing the same amount of zinc and 1 per cent lead. This is shown in Figs. 27 and 28 of specimens with 2 per cent zinc and no lead, and with 2 per cent zinc and 1 per cent lead, respectively.

3. Plugs containing zinc and lead, and which had been in service for periods of from 4 to 12 months did not develop this structure; indeed, in most cases neither the zinc nor the lead could be detected with certainty in their microstructure. This was true, for example, of plug No. 1035, containing 1.8 per cent zinc and 0.1 per cent of lead, which had been in service 3 months and was still absolutely sound.

It seems then that the progress of the "network" oxidation is dependent upon the previous presence of the coalesced network zinc-tin structure, and if for some reason the zinc is present in another form of distribution the oxidation can not proceed in this manner.

Upon heating with water in the autoclave no difference could be noticed in the behavior of the sound, i. e., unoxidized, and the plugs oxidized before pouring.

III. TESTING OF THE PURITY OF TIN

It is suggested that the use of a high-grade tin of the purity of Banka, Straits, Pyrmont, or Williams, Harvey & Co., refined (see analyses by Cowan, Appendix 1), would eliminate the danger of deterioration by oxidation of the fillings of tin plugs. Of these varieties, Banka is undoubtedly the most consistently pure, although some samples of other varieties were of almost equal purity—for example, Williams, Harvey & Co., refined. It would seem safest, therefore, to require a tin in such plugs to be 99.9 per cent pure and to contain less than 0.01 per cent each of zinc

and lead. This would admit Banka tin and some lots of other varieties. It has, however, been in the past year impossible at times to obtain Banka tin on the market. For such a contingency provision must be made for admitting other and slightly poorer tins. If the specifications called for tin of 99.8 per cent purity, containing less than 0.05 per cent lead and less than 0.01 per cent zinc, most of the high-grade tins would be included, and such tin, with the higher lead content, would probably be as safe for use in plugs as the former, as there is as yet no evidence that a lead content of even 0.1 per cent is harmful in such plugs.

Frequent tests by chemical analysis must be made of the purity of the tin bought under such specifications as those recommended above. It can be seen from Table 2 that such analysis may be limited in most cases to a determination of zinc and lead, which seem to be the principal impurities.

A somewhat quicker method of determining whether or not a tin sample is pure is given in the determination of its melting point. Table 3 is given below, in which the lowering of the melting point of tin for 1 per cent of various ordinary metallic impurities has been calculated from the results of thermal analysis of these alloys by various investigators (see Bornemann, 1909–1912). The rough assumption has been made in these calculations that the liquidus curve is linear.

TABLE 3

Effect of Impurities on Melting Point of Tin

Metal	Tin containing—	Melting point	Lowering of melting point per 1 per cent of metal calculated
	Per cent	°C	°C
Antimony	7.5	240	+ 1.0
Bismuth	5.5	225	− 1.2
Iron	2.0	300	+30.0
Lead	2.5	225	− 2.8
Zinc	3.0	225	− 2.3

It is seen that small amounts of impurities may in general be readily detected although the simultaneous presence of metals, such as antimony and zinc, in proper amounts might give an alloy having a melting point equal to that of pure tin. In the samples analyzed the only impurities found in appreciable amounts were zinc and lead, each of which lowers the melting point. Therefore the determination of the melting or freezing point of the tin may be accepted as a useful and rapid test of its purity. It may be noted that extremely small amounts of lead and zinc of the order of magnitude of 0.02 or 0.03 per cent can not be detected by such

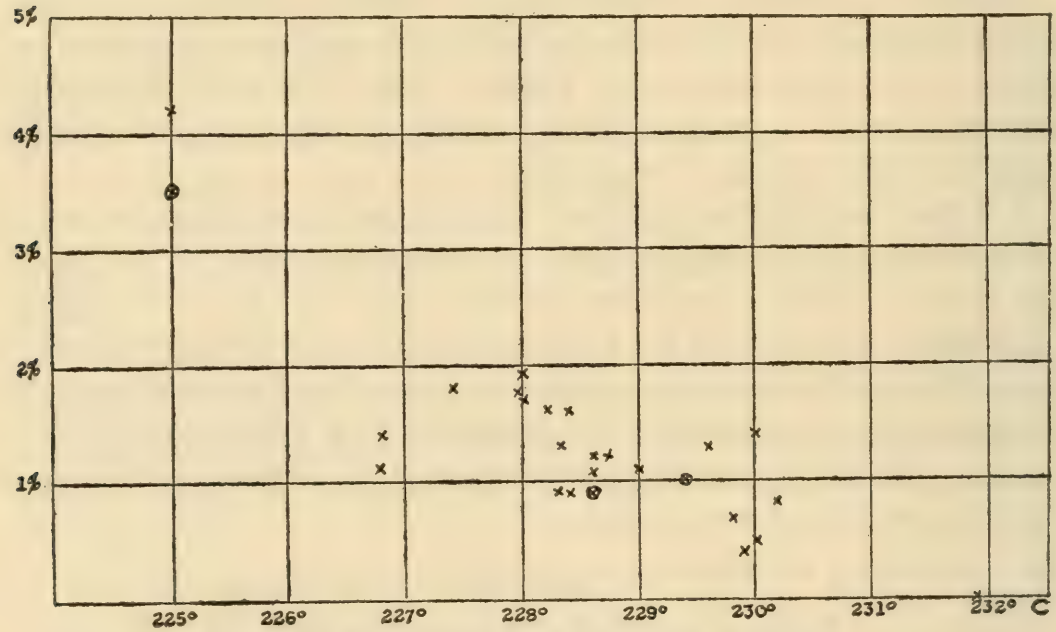

FIG. 29.—*Effect of small quantities of lead and zinc upon freezing point of tin*

a thermal method and it is also not possible to distinguish with certainty between "Kahlbaum," Banka, and Straits tin by the ordinary determination of the melting point as made by the cooling curve method.

In Fig. 29 are plotted the melting points of all of the tin specimens analyzed, as a function of the percentage of the two impurities, lead and zinc. In order to avoid using three coordinates, it was roughly assumed, from the table above, that 1 per cent lead was equal in effect to 1.1 per cent zinc and the sum of the zinc content and of the lead content multiplied by 1.1 was plotted as ordinates. This is equivalent to assuming that the effects of zinc and lead

upon the lowering of the freezing point of tin are additive, or that the ternary liquidus surface for small lead and zinc contents is formed by the motion of a straight line. From this curve an approximate estimate may be made of the amount of combined zinc and lead in a tin which contains these two impurities only.

IV. CONCLUSIONS

The fact that stands out most strongly throughout this investigation is that zinc should not be present in the tin fillings of fusible plugs. The lowest zinc content actually found in any of the four plugs analyzed, which displayed the "network" type of oxidation, was 0.3 per cent, but this can not be accepted as the actual lowest value of the zinc content at which oxidation can take place. Furthermore, although zinc is, because of its greater corrodability, most dangerous when coalesced into a network structure such as is developed upon heating at about 180°, other metals which do not form solid solution with tin may also cause the formation of this structure, as, for instance, lead. It seems then that in such plugs tin must be used which is as free as possible from zinc and lead. This statement is made notwithstanding the apparent fact that if zinc is present a small content of lead is actually beneficial; it appears better, however, to prevent this oxidation by using pure tin rather than by adding lead in case the tin already contains zinc.

A consideration of the results of the tin analyses by Cowan, given in Appendix 1, shows that it is possible to get Banka and other tin which contains only traces of zinc and at the utmost 0.010 per cent of lead. It is highly probable that the use of tin of such purity would eliminate the danger of oxidation of the "network" type.

With the exception of plug No. 122, which had a melting point of 231.9° C, and in which the formation of nonmetallic inclosures had not proceeded by natural means, as shown above, the plugs of the 5 (b) class (i. e., with inclusions of solid oxide at the fire end) all contained impurities, probably to the extent of about 1 to 1.5 per cent. The inference is, therefore, that oxidation of the tin in service would cease with the introduction of the use

of a tin of purity equal to that of Banka, probably also of tin of purity equal to that of Straits or Pyrmont. Observations are made above regarding the testing of the purity of tin.

However, one question may be raised. A leaky plug will always be a temptation to careless practice on the part of the engineer in charge. He may stop them up instead of replacing them. Now, the chances that leaks may develop in a plug are fairly large. The coefficient of expansion per degree centigrade of the material of a casing will be around 0.000020, whereas that of tin is about 0.000023. Tin undergoes an allotropic change at about 160° C, accompanied by a change of volume of about 0.03 per cent. Therefore, opportunity is constantly given for interplay between plug filling and casing during temperature changes. A number of plugs which had been in service were removed because of leaking.

Considering now the three sets of specifications (Appendixes 2 and 3), it is seen that any set of specifications such as those of the Interstate Commerce Commission, which totally ignore the question of the purity of the tin, are insufficient. The specifications of the American Society of Mechanical Engineers seem to limit the quality of the tin in calling for tin of a melting point between 400° and 500° F, but in reality this specification has no significance from the standpoint of the purity of the tin, since it would admit tin containing as much as 65 per cent of lead or 15 per cent of zinc. Manifestly such a specification is worthless. The Steamboat Inspection Service requires at present "Banka tin," but propose to amend this paragraph to call for "tin 99.7 per cent pure, containing not more than 0.1 per cent of lead and not more than 0.1 per cent of zinc." The latter is doubtless a more practical specification than the former, but there is no doubt but that better tin than this can and should be obtained for such plugs, as shown in Section III.

The requirement of the Interstate Commerce Commission that fusible plugs "be removed and cleaned of scale once every month" is desirable, since, as above demonstrated, an impure plug may begin to show visible signs of deterioration after only 500 hours' service. A combination of test of purity of new plugs from each heat cast with frequent inspections or discarding of plugs would appear to be the safest practice.

In view of the fact that many manufacturers are not furnishing pure tin for fusible boiler plugs, and it having been shown above that impure tin may be dangerous, it would probably be desirable, in the interests of safety, to license a few manufacturers whose product could be rigidly controlled by Federal inspection.

1. SUMMARY

1. An explanation has been sought for the "failure" by oxidation of fusible tin boiler plugs during service. These failures are of two types—(*a*) those in which the oxide forms as an interlocking "network" throughout the tin of the filling; (*b*) those in which the oxide forms as a solid hard mass at the fire end of the plug.

2. About 950 new and 100 used plugs were examined, the latter classified according to the type of change or deterioration which had taken place in them during service, and a number were tested for purity of the tin, both by determination of the melting point of the latter, and by chemical analysis. Lead and zinc were found to be the principal impurities present.

3. An explanation for the formation of the "network" type of oxidation is found in the presence of zinc in amounts varying from 0.3 to 4 per cent.

4. The conclusion is drawn that, since all plugs examined, which were "dangerous," contained impurities, the use of pure tin of the quality of Banka, of Williams, Harvey & Co., refined, or even of Straits or Pyrmont (see Appendix 1) would probably eliminate the danger of oxidation of these plugs in service.

5. The relation of these findings to existing specifications for fusible plugs is discussed and more rigorous inspection of the product of licensed manufacturers suggested.

A. B. Lort, of the chemical division, made all of the quantitative and most of the qualitative chemical analyses for this investigation, and to him, as well as to R. W. Woodward, R. G. Waltenberg, C. P. Karr, and A. S. McCabe, for their aid in this work, the authors' thanks and appreciation are here expressed.

The material for this investigation was furnished by the Steamboat Inspection Service, as noted above.

WASHINGTON, May 28, 1915.

APPENDIXES

APPENDIX 1.—ANALYSES OF PIG TIN BY COWAN

Analyses are here given of series of brands of tin by W. A. Cowan (Journal of the American Institute of Metals, 1914).

Comparison—Pig Tin Analyses

[A=American Sheet & Tin Plate Co.; B=Ledoux & Co.; C=A. H. Knight; D=National Lead Co.]

BANKA

	A	B	C	D
	Per cent	Per cent	Per cent	Per cent
Lead	Trace	0.010	Trace	Trace
Arsenic	0.024	0.004	Trace	None
Antimony	0.038	None	0.006	0.006
Copper	0.003	0.009	0.002	0.004
Cadmium	.....	None	.....	None
Bismuth	.....	0.002	Nil	None
Iron	Trace	0.004	0.023	0.019
Zinc	Trace	.....	.....	Trace
Ni and Co	.....	None	Nil	None
Manganese	.....	None	.....	None
Tungsten	.....	.....	.....	None
Sulphur	Trace	.....	Trace	Trace
Phosphorus	Trace	None	Nil	0.008
Tin	[a] 99.935	[a] 99.971	99.963	[a] 99.963
Total	100.000	100.000	99.994	100.000

STRAITS

Lead	0.057	0.080	0.049	0.064
Arsenic	0.084	0.072	0.058	0.077
Antimony	0.103	None	0.018	0.018
Copper	0.013	0.027	0.020	0.020
Cadmium	.....	None	.....	None
Bismuth	.....	0.003	0.004	None
Iron	Trace	0.005	0.003	0.005
Zinc	Trace	.....	.....	0.015
Ni and Co	.....	None	Nil	None
Manganese	.....	None	.....	None
Tungsten	.....	.....	.....	None
Sulphur	Trace	.....	Trace	0.009
Phosphorus	Trace	None	Nil	0.010
Tin	[a] 99.743	[a] 99.813	99.831	[a] 99.782
Total	100.000	100.000	99.983	100.000

[a] By difference.

FIG. 2.—*Original plug showing tin (light) and tin oxide. Magnification =½*

FIG. 3.—*Used plug with filling partially melted out. Magnification =½*

FIG. 4.—*Used plug with filling partially melted out. Magnification =½*

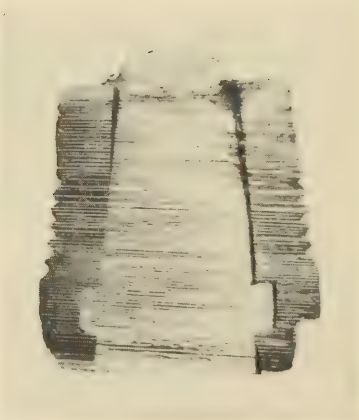

FIG. 5.—*Used plug showing swelled filling. Magnification =½*

FIG. 6.—*Used plug showing swelled filling. Magnification* $=\frac{1}{2}$

FIG. 7.—*Used plug showing oxide layer between filling and casing. Magnification* $=\frac{1}{2}$

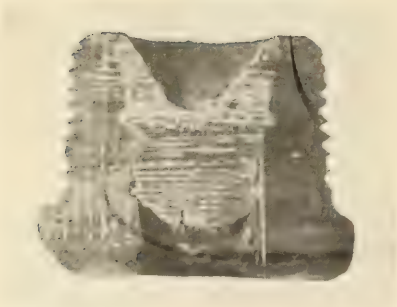

FIG. 8.—*Used plug. Magnification* $=\frac{1}{2}$

FIG. 9.—*Used plug showing network type of oxidation. Magnification* $=\frac{1}{2}$

FIG. 10.—*Used plug showing network type of oxidation. Magnification =½*

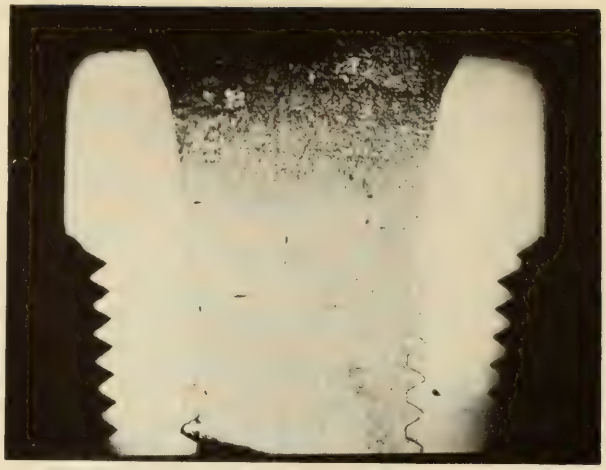

FIG. 11.—*Used plug showing network type of oxidation. Magnification =1*

FIG. 12.—*Used plug showing network type of oxidation. Magnification =½*

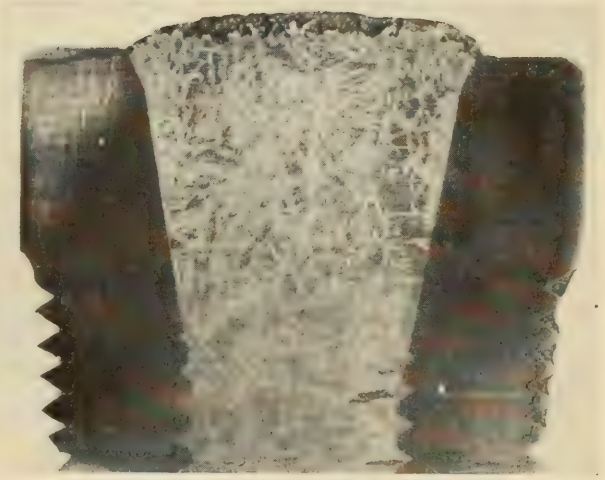

FIG. 13.—*Used plug, showing network type of oxidation. Magnification =1*

FIG. 14.—*Used plug showing solid "oxide" inclusions at fire end. Magnification =½*

FIG. 15.—*Used plug showing solid "oxide" inclusions at fire end. Magnification =½*

FIG. 16.—*Used plug showing solid "oxide" inclusions at fire end. Magnification =½*

FIG. 17.—*Used plug showing solid "oxide" inclusions at fire end. Magnification =½*

FIG. 18.—*Used plug showing solid "oxide" inclusions at fire end. Magnification =½*

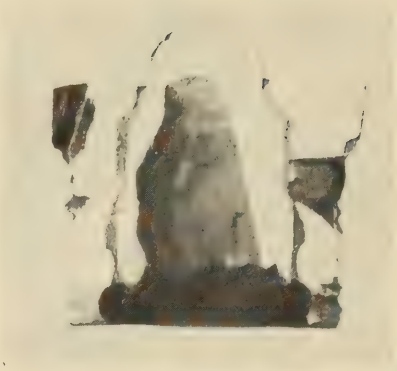

FIG. 19.—*Used plug. Magnification =½*

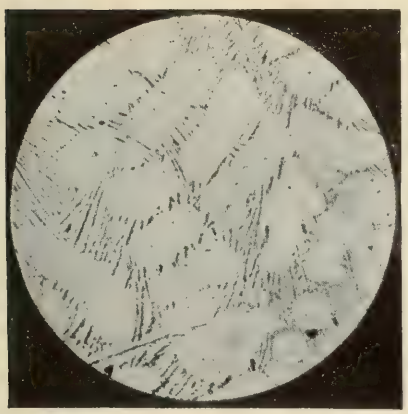

FIG. 21.—*Structure of zinc-tin alloy with 1 per cent zinc, slowly cooled. Magnification =100, reduced to 45 in printing*

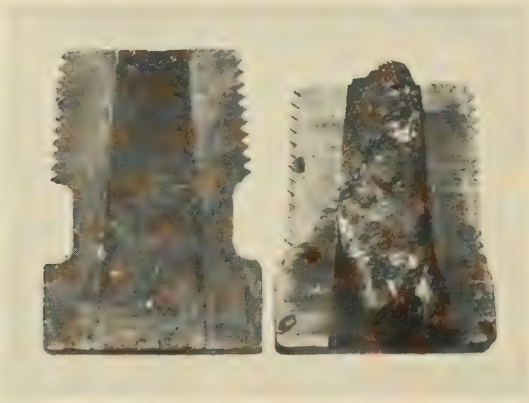

FIG. 22.—*Shows the two halves of a plug containing lead; the left half is as received (unused), the right half has been treated in water under pressure at about 180° C. Magnification =½*

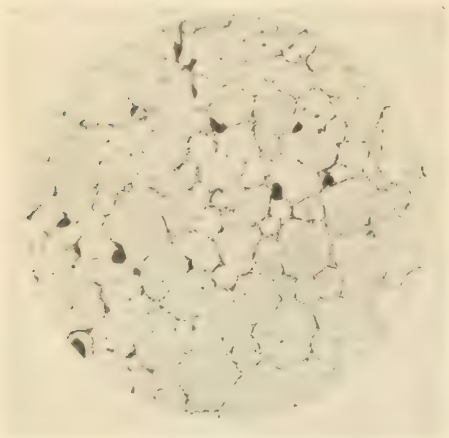

FIG. 23.—*This photomicrograph shows microstructure of heated half of plug shown in Fig. 22. Magnification =20, reduced to 9 in printing*

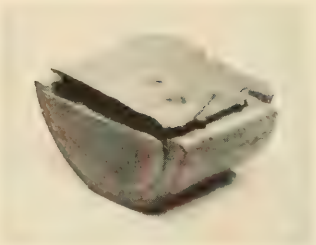

FIG. 24.—*This half plug has cracked as shown upon heating with water at 180° C. The plug contains zinc. Magnification =½*

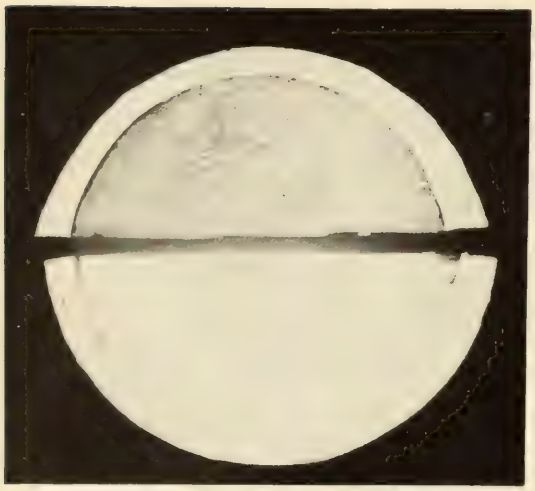

FIG. 25.—*Two halves of a plug containing 0.5 per cent zinc. The upper half has been heated for 500 hours from 180° to 195° C.; the lower half is as received. Magnification =1*

FIG. 26.—*Same as Fig. 25; center section of the heated half*

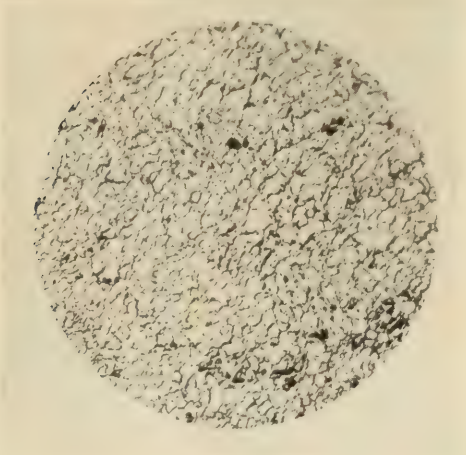

FIG. 27.—*Photomicrograph shows structure of plug containing 2 per cent zinc and no lead after treating with water in autoclave for 500 hours at about 180° C. Magnification =15, reduced to 7 in printing*

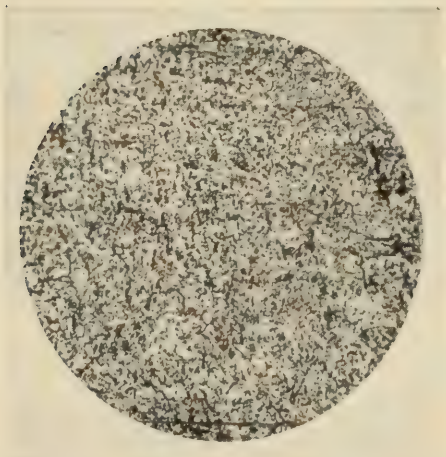

FIG. 28.—*Photomicrograph shows structure of plug containing 2 per cent zinc and 1 per cent lead, heated as in Fig. 27. Magnification =15, reduced to 7 in printing*

PYRMONT (AUSTRALIAN)

	A	B	C	D
	Per cent	Per cent	Per cent	Per cent
Lead	0.019	0.045	0.016	0.045
Arsenic	0.020	0.035	0.019	0.038
Antimony	0.054	0.074	0.051	0.098
Copper	0.023	0.027	0.015	0.024
Cadmium	.....	None	.....	None
Bismuth	.....	0.010	0.007	None
Iron	Trace	0.003	0.003	0.003
Zinc	Trace	.....	.....	0.010
Ni and Co	.....	None	Nil	None
Manganese	.....	None	.....	None
Tungsten	.....	.....	.....	None
Sulphur	Trace	.....	Trace	Trace
Phosphorus	Trace	None	Nil	0.020
Tin	[a] 99.784	[a] 99.806	[a] 99.866	[a] 99.762
Total	100.000	100.000	99.977	100.000

WILLIAMS, HARVEY & COMPANY (ENGLISH)

	Common				Refined	
	A	B	C	D	C	D
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Lead	0.339	0.374	0.380	0.387	Trace	0.010
Arsenic	.038	.078	.060	.077	0.049	.061
Antimony	.336	.220	.215	.252	.032	.039
Copper	.075	.100	.060	.090	.015	.014
Cadmium	.....	None	.....	None	.....	None
Bismuth	.....	.070	.059	.064	.002	None
Iron	Trace	.008	.004	.002	Trace	.003
Zinc	Trace	.....	.....	.006	.....	.012
Ni and Co	.....	None	.007	None	Nil	None
Manganese	.....	None	.....	None	.....	None
Tungsten	.....	.....	.....	None	.....	None
Sulphur	Trace	.....	.002	.006	Trace	Trace
Phosphorus	Trace	None	Trace	.007	Nil	Trace
Tin	[a] 99.212	[a] 99.150	99.260	[a] 99.109	99.920	[a] 99.861
Total	100.000	100.000	100.047	100.000	100.018	100.000

[a] By difference.

APPENDIX 2. EXISTING SPECIFICATIONS FOR FUSIBLE TIN BOILER PLUGS

At their annual meeting, January to March, 1915, the board of supervising inspectors, Steamboat-Inspection Service, proposed the following specifications to supersede those already in force, adopted in December, 1914:[5]

FUSIBLE PLUGS

SECTION 20, ocean and coastwise; lakes, bays, and sounds; and rivers. (Amended.)

20. Fusible plugs for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service shall be madeof a bronze casing *with the bore tapering continuously and evenly from end to end, and* filled from end to end with [good, pure Banka] tin [with a continuous taper from end to end of filling. The bore of the plug may be lightly threaded for a part or all of its length if deemed necessary to retain the filling in the plug under pressure, but no counterbore, recess, or cavity other than a thread will be allowed] *not less than 99.7 per cent pure and to contain not more than 0.1 per cent of lead and not more than 0.1 per cent of zinc. The small end of the bore may be countersunk not more than one thirty-second of an inch in depth and width, but no recess, thread, or cavity other than this countersink shall be allowed.*

Fusible plugs, except those which are hereafter provided for, shall have an external diameter of not less than three-fourths of an inch pipe tap, and the [Banka tin] filling shall be at least one-half of an inch in diameter at the smaller end, and shall have a larger diameter at the opposite end of the plug: *Provided, however,* That all fusible plugs fitted in boilers carrying a steam pressure exceeding 150 pounds to the square inch may be reduced at the smaller end of the [Banka tin] filling to five-sixteenths of an inch in diameter.

Every boiler other than boilers of the water-tube type shall be fitted with at least two fusible plugs as described above, and located as follows:

Upright boilers shall be fitted with two fusible plugs of an external diameter of not less than three-eighths of an inch pipe tap, the [Banka tin] filling to be at least one-fourth of an inch in diameter at the smaller end and shall have a greater diameter at the opposite end. The fusible plugs shall be located in separate tubes not more than 2 inches below the lowest gauge cock [, but in such boilers having a cone top the plugs shall be inserted in the upper sheet].

Externally heated cylindrical boilers, with flues, shall have one plug in the top of the upper flue, not more than 4 feet from the back end of the flue, and shall also have a plug fitted to the shell of the boiler immediately below the fire line and not less than 4 feet from the front end: *Provided, however,* That when the flues are not more than 6 inches in diameter fusible plugs of not less diameter than three-eighths of an inch pipe tap may be used in such flues.

Fire box, scotch, and other types of shell boilers not specially provided for, having a combustion chamber common to all furnaces, shall have two plugs fitted to the crown sheet and not more than 12 inches apart. Boilers fitted with separate combustion

[5] The parts of the rules struck out are inclosed in brackets [thus], while the addition to the rules are printed in *italic*.

chambers shall be fitted with a fusible plug in the center of the crown sheet of each chamber.

Boilers of types not herein provided for shall be fitted with at least two fusible plugs of such dimensions and located in such parts of the boiler as will, in the judgment of the local inspectors, best meet the purposes for which they are intended.

Fusible plugs shall be renewed after six months of service, and the inspector of boilers shall assure himself at each annual inspection by personal examination and by testing the ends of the filling by filing to determine its condition that the plugs are in good and serviceable condition.

Fusible plugs shall be so fitted that the smaller end of the [Banka tin] filling is exposed to the fire, and shall be at least 1 inch higher on the water side than the plate or flue in which they are fitted.

Notwithstanding anything which may be contained in this rule, fusible plugs shall be so fitted that the end of the [Banka tin] *filling* on the water end of the plug is not less than 1 inch above the dangerous low-water level.

Manufacturers of fusible plugs shall stamp their name or initials thereon for identification and shall file with the Supervising Inspector General of the Steamboat-Inspection Service at Washington, D. C., a certificate duly sworn to that such plugs are filled with [good, pure Banka] tin [free from scoriae or oxides] *of the character required by this rule* and made in accordance [with this rule] *therewith,* and shall also furnish him a sample plug for each lot of [50] *100* plugs or less and a proportionate number of samples for larger lots [, such sample plugs to be split evenly from end to end so that the construction may be observed].

Each manufacturer of fusible plugs shall number all plugs in accordance with the number of the heat from which the plugs were filled. For instance, the first pouring shall be number one, and all plugs filled from this heat shall be numbered 1; the next pouring shall be numbered 2, etc. The samples furnished the Supervising Inspector General shall bear the same number for any one heat and shall be part of the heat from which the plugs represented by the sample are poured.

The heat number shall be plainly stamped on each end of filling with numbers not less than one-twelfth inch in height.

The manufacturer's name or initials shall be plainly stamped on the larger end or face of the casing.

One sample plug shall be furnished from each heat of [50] *100* plugs or less. For [over 50] *more than 100* and not [over 100] *more than 200* plugs of any one heat, two plugs shall be furnished, etc. *Such sample plugs shall not be split as formerly required.*

In transmitting samples of fusible plugs to the Supervising Inspector General, the fusible plugs and the letters of transmittal shall be addressed as follows: "Suprevising Inspector General, Steamboat-Inspection Service, Department of Commerce, Washington, D. C."

One letter of transmittal shall be required for each heat.

In letter of transmittal the following information shall be stated:

Number of heat.

Number of fusible plugs manufactured from the heat.

Number of samples of fusible plugs from the heat transmitted.

Name of manufacturer or initials stamped on casing of plug.

Following is a general form of affidavit to be followed by manufacturers of fusible plugs:

STATE OF ———, *County of* ———.

I hereby certify, on this —— day of ———, 191—, that I am ——— ———, of the
(State owner or name position.)
manufactory of ———, located at ———, in the State of ———; that all fusible plugs furnished for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service by the said manufactory will be filled with [good, pure Banka] tin [free from scoriæ or oxides] *of the character required*, and will be made in accordance with the rules and regulations of the Board of Supervising Inspectors, Steamboat-Inspection Service, governing the manufacture of fusible plugs; and that I am authorized to make this certificate.

——— ———
(Signature of manufacturer.)

Subscribed and ——— to before me this —— day of ———, 191—.
(Sworn or affirmed.)

[NOTARY'S SEAL.] (Signature) ——— ———
Notary Public.

The certificate shall be executed by some person having authority to make the statements contained therein.

The affidavit shall be sent to the Supervising Inspector General.

On receipt of a properly executed affidavit by the Supervising Inspector General, the inspectors of the Steamboat-Inspection Service and the merchant marine generally shall be notified.

In their final report to the American Society of Mechanical Engineers, published in February, 1915, the boiler-code committee included the following specifications for fusible plugs among their "Standard specifications."

REPORT OF THE COMMITTEE TO FORMULATE STANDARD SPECIFICATIONS FOR THE CONSTRUCTION OF STEAM BOILERS AND OTHER PRESSURE VESSELS AND FOR CARE OF SAME IN SERVICE.

FUSIBLE PLUGS.

428. Fusible plugs, if used, shall be filled with tin with a melting point between 400 and 500 degrees Fahrenheit.

429. The least diameter of fusible metal shall be not less than one-half inch, except for maximum allowable working pressures of over 175 pounds per square inch or when it is necessary to place a fusible plug in a tube, in which case the least diameter of fusible metal shall be not less than three-eighths inch.

430. Each boiler may have one or more fusible plugs, located as follows:

(*a*) In horizontal return tubular boilers: In the rear head, not less than 2 inches above the upper row of tubes, the measurement to be taken from the line of the upper surface of tubes to the center of the plug, and projecting through the sheet not less than 1 inch.

(*b*) In horizontal flue boilers: In the rear head, on a line with the highest part of the boiler exposed to the products of combustion, and projecting through the sheet not less than 1 inch.

(*c*) In traction, portable, or stationary boilers of the locomotive type or star water tube boilers: In the highest part of the crown sheet, and projecting through the sheet not less than 1 inch.

(*d*) In vertical fire-tube boilers: In an outside tube, not less than one-third the length of the tube above the lower tube sheet, and projecting through the sheet not less than 1 inch.

(*e*) In vertical fire-tube boilers, Corliss type: In a tube, not less than one-third the length of the tube above the lower tube sheet.

(*f*) In vertical submerged tube boilers: In the upper tube sheet.

(*g*) In water-tube boilers, horizontal drums, Babcock & Wilcox type: In the upper drum, not less than 6 inches above the bottom of the drum, over the first pass of the products of combustion, and projecting through the sheet not less than 1 inch.

(*h*) In Stirling boilers, standard type: In the front side of the middle drum, not less than 4 inches above the bottom of the drum, and projecting through the sheet not less than 1 inch.

(*i*) In Stirling boilers, superheater type: In the front drum, not less than 6 inches above the bottom of the drum, exposed to the products of combustion, and projecting through the sheet not less than 1 inch.

(*j*) In water-tube boilers, Heine type: In the front course of the drum, not less than 6 inches above the bottom of the drum, and projecting through the sheet not less than 1 inch.

(*k*) In Robb-Mumford boilers, standard type: In the bottom of the steam and water drum, 24 inches from the center of the rear neck, and projecting through the sheet not less than 1 inch.

(*l*) In water-tube boilers, Almy type: In a tube or fitting exposed to the products of combustion.

(*m*) In vertical boilers, Climax or Hazelton type: In a tube or center drum not less than one-half the height of the shell, measuring from the lowest circumferential seam.

(*n*) In Cahall vertical water-tube boilers: In the inner sheet of the top drum, not less than 6 inches above the upper tube sheet, and projecting through the sheet not less than 1 inch.

(*o*) In Wickes vertical water-tube boilers: In the shell of the top drum and not less than 6 inches above the upper tube sheet, and projecting through the sheet not less than 1 inch; so located as to be at the front of the boiler and exposed to the first pass of the products of combustion.

(*p*) In Scotch-marine type boilers: In the combustion chamber top, and projecting through the sheet not less than 1 inch.

(*q*) In dry back Scotch type boilers: In the rear head, not less than 2 inches above the upper row of tubes, and projecting through the sheet not less than 1 inch.

(*r*) In economic type boilers: In the rear head, above the upper row of tubes.

(*s*) In cast-iron sectional-heating boilers: In a section over and in direct contact with the products of combustion in the primary combustion chamber.

(*t*) In water-tube boilers, Worthington type: In the front side of the steam and water drum, not less than 4 inches above the bottom of the drum, and projecting through the sheet not less than 1 inch.

(*u*) For other types and new designs, fusible plugs shall be placed at the lowest permissible water level, in the direct path of the products of combustion, as near the primary combustion chamber as possible.

In the "Rules and Instructions for Inspection and Testing of Locomotive Boilers and Their Appurtenances" of the division of locomotive boiler inspection of the Interstate Commerce Commission there is found the following paragraph relating to fusible plugs:

14. If boilers are equipped with fusible plugs they shall be removed and cleaned of scale at least once every month.

APPENDIX 3

DEPARTMENT OF COMMERCE,
STEAMBOAT-INSPECTION SERVICE.

General Rules and Regulations prescribed by the Board of Supervising Inspectors, amended January, 1913, and further amended by action of executive committee of the Board of Supervising Inspectors, meetings April 18, July 9, August 16, October 21, and December 10, 1913. (*Amendments approved by the Secretary of Commerce. Edition of January 13, 1914.*)

FUSIBLE PLUGS.

21. Every boiler, other than boilers of the water-tube type, shall have at least one fusible plug as described below. Plugs shall be made of a bronze casing filled with good Banka tin tapering straight from end to end of filling. The manufacturers of fusible plugs shall stamp their name or initials thereon for identification, and shall file with the local inspectors a certificate, duly sworn to, that such plugs are filled with Banka tin and made in accordance with this rule.

Fusible plugs, except as otherwise provided for, shall have an external diameter of not less than three-fourths of an inch pipe tap, and the Banka tin shall be at least one-half of an inch in diameter at the smaller end and shall have a larger diameter at the opposite end of the plug: *Provided, however,* That all plugs used in boilers carrying a steam pressure exceeding 150 pounds to the square inch may be reduced at the smaller end of the Banka tin to five-sixteenths of an inch in diameter.

Fusible plugs, when used in the tube of upright boilers, shall have an external diameter of not less than three-eighths of an inch pipe tap, and the Banka tin shall be at least one-fourth of an inch in diameter at the smaller end and shall have a greater diameter at the opposite end of the plug.

Externally heated cylindrical boilers, with flues, shall have one plug inserted in one flue, and also one plug inserted in shell of each boiler immediately below the fire line and not less than 4 feet from the front end: *Provided, however,* That when such flues are not more than 6 inches in diameter, a fusible plug of not less diameter than three-eighths-inch pipe tap may be used in such flues.

Other shell boilers, except especially provided for, shall have one plug inserted in the crown sheet of the back connection.

Vertical tubular boilers shall have one plug inserted in one of the tubes at least 2 inches below the lowest gauge cock, but in boilers having a cone top the plug shall be inserted in the upper tube sheet.

All plugs shall be inserted so that the small end of the Banka tin shall be exposed to the fire.

It shall be the duty of the inspector at each annual inspection to see that the plugs are in good condition. (Sec. 4418, R. S.)

DEPARTMENT OF COMMERCE,
STEAMBOAT-INSPECTION SERVICE,
Washington, June 30, 1914.

CIRCULAR LETTER.

United States Supervising and Local Inspectors,
Steamboat-Inspection Service, Manufacturers of Fusible Plugs,
Owners of Steam Vessels, and others concerned:

Under the provisions of section 4405, Revised Statutes of the United States, as amended by the act of Congress approved February 8, 1907, the executive committee of the Board of Supervising Inspectors, Steamboat-Inspection Service, at a meeting held in New York, N. Y., on June 22, 1914, adopted the following resolution:

Resolved, That section 21, Rule II, page 44, of the General Rules and Regulations prescribed by the Board of Supervising Inspectors, as amended January, 1913, edition of January 13, 1914, be struck out and the following substituted therefor:

FUSIBLE PLUGS.

21. Fusible plugs for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service shall be made of a bronze casing filled with good, pure Banka tin tapering evenly from end to end of filling.

Fusible plugs, except those which are hereafter provided for, shall have an external diameter of not less than three-fourths of an inch pipe tap, and the Banka tin filling shall be at least one-half of an inch in diameter at the smaller end, and shall have a larger diameter at the opposite end of the plug: *Provided, however*, That all fusible plugs fitted in boilers carrying a steam pressure exceeding 150 pounds to the square inch may be reduced at the smaller end of the Banka tin filling to five-sixteenths of an inch in diameter.

Every boiler other than boilers of the water-tube type shall be fitted with at least two fusible plugs, as described above, and located as follows:

Upright boilers shall be fitted with two fusible plugs of an external diameter of not less than three-eighths of an inch pipe tap, the Banka tin filling to be at least one-fourth of an inch in diameter at the smaller end and shall have a greater diameter at the opposite end. The fusible plugs shall be located in separate tubes not more than 2 inches below the lowest gauge cock, but in such boilers having a cone top the plugs shall be inserted in the upper tube sheet.

Externally heated cylindrical boilers, with flues, shall have two plugs in the top of the upper flue, one of the plugs to be not more than 4 feet from the back end of the flue and the other to be placed about the middle of the length of the flue, and shall also have a plug fitted to the shell of the boiler immediately below the fire line, and not less than 4 feet from the front end: *Provided, however*, That when the flues are not more than 6 inches in diameter fusible plugs of not less diameter than three-eighths of an inch pipe tap may be used in such flues.

Fire-box, Scotch, and other types of shell boilers not specially provided for shall have three plugs fitted to the crown sheet of the combustion chamber, one to be fitted about 12 inches inboard on each end of the crown and one in the center. Boilers fitted with separate combustion chambers shall be fitted with a fusible plug in the center of the crown sheet of each chamber.

Boilers of types not herein provided for shall be fitted with at least two fusible plugs of such dimensions and located in such parts of the boiler as will, in the judgment of the local inspectors, best meet the purposes for which they are intended.

Fusible plugs shall be renewed after four months of service, and the inspector of boilers must assure himself, by personal observation and by testing with a file to determine the character of the filling at each annual inspection, that they are in good condition.

Fusible plugs shall be so fitted that the smaller end of the Banka tin is exposed to the fire, and shall be at least 1 inch higher on the water side than the plate or flue in which they are fitted.

Notwithstanding anything which may be contained in this rule, fusible plugs shall be so fitted that the end of the Banka tin on the water end of the plug is not less than 1 inch above the dangerous low-water level.

Manufacturers of fusible plugs shall stamp their name or initials thereon for identification, and shall file with the Supervising Inspector General of the Steamboat-Inspection Service at Washington, D. C., a certificate duly sworn to that such plugs are filled with good, pure Banka tin free from scoriæ or oxides, and made in accordance with this rule, and shall also furnish him a sample plug for each lot of 20 plugs or less, and a proportionate number of samples for larger lots.

This action of the executive committee received the approval of the Secretary of Commerce on June 25, 1914, under the provisions of sections 4405 and 4491, Revised Statutes, and has now the force of law.

In pursuance of the provisions of the above resolution, the following instructions are required to be observed by manufacturers of fusible plugs for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service.

Each manufacturer of fusible plugs will number all plugs in accordance with the number of the heat from which the plugs were filled. For instance, the first pouring after this rule takes effect will be number one, and all plugs filled from this heat will be numbered 1. The next pouring will be number two, and all the plugs filled from this heat will be numbered 2, etc. The samples furnished the Supervising Inspector General must bear the same number for any one heat and must be a part of the heat from which the plugs represented by the sample are poured.

The heat number will be plainly stamped on each end of filling with numbers not less than one-twelfth inch in height.

The manufacturer's name or initials will be plainly stamped on the larger end or face of the casing.

One sample plug will be furnished from each heat of 20 plugs or less. For over 20 and not over 40 plugs or any one heat two plugs will be furnished, etc.

In transmitting samples of fusible plugs to the Supervising Inspector General, the fusible plugs and the letters of transmittal will be addressed as follows: "Supervising Inspector General, Steamboat-Inspection Service, Department of Commerce, Washington, D. C."

One letter of transmittal will be required for each heat.

In letter of transmittal the following information will be stated:

Number of heat.

Number of fusible plugs manufactured from the heat.

Number of samples of fusible plugs from the heat transmitted.

Name of manufacturer, or initials, stamped on casing of plug.

Following is a general form of affidavit to be followed by manufacturers of fusible plugs:

STATE OF ———, *County of* ———.

I hereby certify, on this —— day of ——— 191—, that I am ——— ———, of the
(State owner, or name position.)
manufactory of ——— located at ——— in the State of ———; that all fusible plugs furnished for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service by the said manufactory will be filled with good, pure Banka tin free from scoriæ or oxides, and will be made in accordance with the rules and regulations of the board of supervising inspectors, Steamboat-Inspection Service, governing the manufacture of fusible plugs; and that I am authorized to make this certificate.

——— ———
(Signature of manufacturer.)

Subscribed and ——— to before me this —— day of ———, 191—.
(Sworn or affirmed.)

(Signature) ———

[NOTARY'S SEAL.] *Notary Public.*

The certificate must be executed by some person having authority to make the statements contained therein.

The affidavit must be sent to the Supervising Inspector General.

On receipt of a properly executed affidavit by the Supervising Inspector General, the inspectors of the Steamboat-Inspection Service and the merchant marine generally will be notified.

All fusible plugs at present in stock must be refilled in accordance with the rule of the Board of Supervising Inspectors and the instructions contained herein.

The rule is effective on and after June 25, 1914.

Each board of local inspectors will furnish a copy of this circular letter to each manufacturer of fusible plugs and to each owner of steam vessels in its district.

GEO. UHLER,
Supervising Inspector General.

Approved June 30, 1914.
WILLIAM C. REDFIELD,
Secretary of Commerce.

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[Continued from page 2 of cover]

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